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A BACKGROUND FOR THE QUANTUM THEORY

by

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for

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THE NATURE OF LIGHT AND MATTER:
A BACKGROUND FOR THE QUANTUM THEORY

The purpose of this paper is to recount some of the greater discoveries in physics. Both the theoretical and the experimental contributions will be described--contributions that bear directly on the two main questions that prompted the new quantum theory. The questions are, "What is matter?", and, "What is light?"

I. The early optics--seventeenth century
   - A. Grimaldi and Hooke
   - B. Newton's experiments, physical optics
   - C. Newton's Queries
   - D. Huygens' longitudinal wave theory

II. Nineteenth century developments (to 1887)
   - A. Young's experiment
   - B. Fresnel's theoretical, experimental work
   - C. Foucault and the speed of light
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III. The photoelectric effect and related phenomena
   - A. Hertz' test--discovery
   - B. Hallwachs, Stoletow--nature of the discharge
   - C. Lenard--similarity to cathode rays

III. The photoelectric effect and related phenomena, cont'd.

D. Thomson: nature of the cathode rays

E. Millikan: the value of e

IV. The old quantum theory and its supports

A. Two black-body radiation laws

B. Planck's quantum theory for radiation

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A. De Broglie waves

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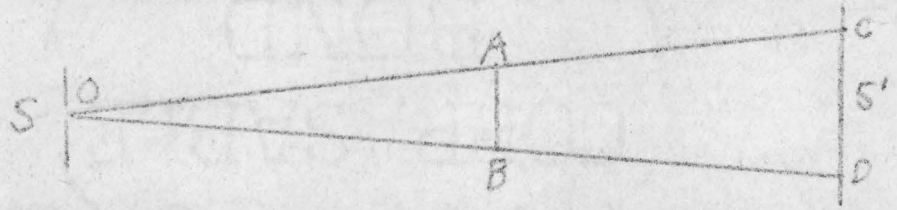
Physicists made the first major advances toward knowing the nature of light in the seventeenth century. Grimaldi published one of the earliest papers on physical optics in the year 1665. Some of his experiments dealt with the passage of light through small openings.



Light from a small hole at O was blocked by the opaque object AB. Instead of a shadow CD at S', Grimaldi observed a wider shadow. Furthermore, there were parallel colored fringes bordering on the shadow. He found that the smaller the hole, the wider the fringes. Here was an exception to the rule that light traveled in straight lines. Grimaldi had discovered it and he named the Phenomenon "diffraction". Later, he experimented with polished metal reflectors ruled with closely-spaced lines. He found that they, too produced diffraction bands.

Soon afterward, Hooke reported finding colored fringes produced by light reflected from thin liquid layers. He suggested that light itself might be caused from vibrations of particles in the material source.

Isaac Newton began experimenting with prisms about 1666. Some of his findings were published in 1672. The experiments were extensive, beyond anything accomplished before them. Many others had observed the continuous

spectrum of the sun. Newton was the first to note that each spectral color was related to its "refrangibility" (degree of refraction). He sent each color through a second prism and showed that the refraction of a particular color was always the same amount. At the same time, it was evident that colors in the spectrum could not each be broken down into other colors. Thus color was a fundamental property of light itself.

Newton repeated Grimaldi's diffraction experiments, using a human hair as the opaque object. The shadows at varying distances from the hair were bordered by colored fringes: the nearest fringe was violet, and the most-removed fringe was red. Newton did other experiments, passing light through the narrow slits between two knives. He noted that the fringes due to a wedge-shaped slit were hyperbolae. Again, red light was diffracted more than violet. Using monochromatic light from a prism, he still observed fringes, but they were all of one color. Newton believed that diffraction could be explained by some kind of repulsion between the bodies of light and the material in the opaque objects near which light passed. He was reluctant to propose his own theory on the nature of light. Later, he made criticisms of the ideas proposed by Huygens and others of that time. Newton often stated that it was his business to make observations, not to spend his time in speculations. Certainly he made many observations and

reported them in his writings. It is the "Queries" found at the end of Newton's Third Book in Opticks that reveal his thinking on the nature of light.[1] Still, he was reluctant to admit that he favored any theory unproved by experiment. He attributed color to waves in the ether. These waves would in some way be caused by corpuscles. Newton had experimented extensively with lenses and mirrors. It would seem natural to adopt a corpuscular model of light to visualize the propogation of the rays through air, through lenses, and toward and away from reflecting surfaces. A "small body" of light was easy to think about and it accounted for most observations in physical optics.

Christian Huygens in 1678 proposed a longitudinal-wave model of light. Propogation in space, reflection, and refraction of light were clearly explained by waves. The wave theory required a decreased speed of light when traveling in more dense materials. A corpuscle obeying mechanical laws would have to speed up to account for the observed refraction. Neither Newton's particles nor Huygens' waves could account for the polarization of light. Newton himself suggested that one would need a wave "with sides" to explain this effect. "Query 28" states his objections to the wave theory for its failure to explain

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[1] Isaac Newton, Opticks (Based on the 4th edition, London, 1730); New York, 1952, pp. 317-374.

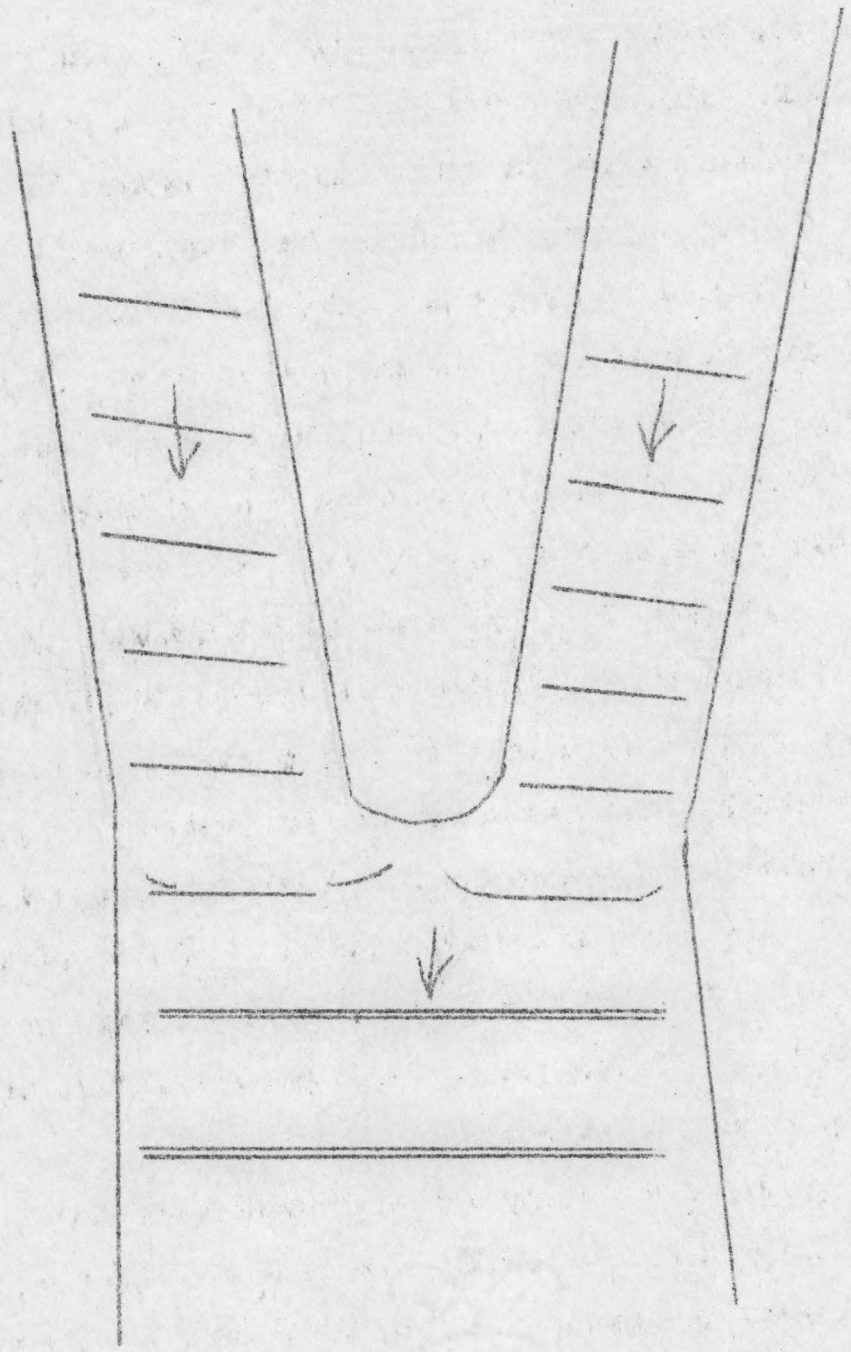


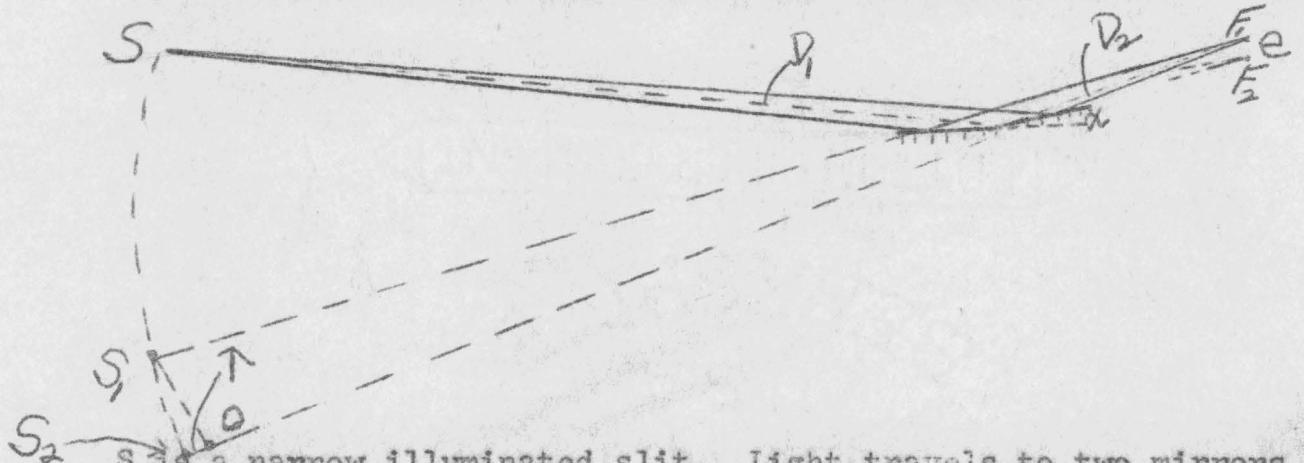
Figure 1. Addition of Waves

double refraction and heating effects. Huygens did not develop a transverse wave theory.

The corpuscular model prevailed for the next century after Newton. There was great need for more experimental evidence concerning the nature of light. Thomas Young found convincing evidence in 1801. His experiments with the interference of light, especially the double-slit experiment, gave new strength to the wave theory. Young passed light from a source through two narrow, closely-spaced openings. He observed the regions of light and dark and explained what he saw in terms of wave motion. The sketch in Figure 1 illustrates his argument. If two channels of water are connected to a common reservoir, we can send waves down each channel. When the waves cross in the reservoir, they may reinforce one another. That will be so when crest meets crest. A more intense wave results. But if crest and trough meet, little or no wave is the result. The light areas correspond to high waves; the dark bands are found where the light waves from the two slits meet crest-to-trough.

A few years after Young's double-slit experiment, Augustin Fresnel did his famous interference experiment with two mirrors arranged at a very small angle. Interference fringes appeared at F, the place where the reflected beams from the two mirrors came together. The

distance between two successive bright fringes can be measured.



S is a narrow illuminated slit. Light travels to two mirrors, inclined at a very small angle α. Monochromatic light is used. D_1 = distance from morror intersection to slit; D_2 = distance from mirror intersection to observer (D_1 much less than D_2); e = distance between central bright fringe and next one adjacent; F_1 and F_2 are the fringes. Only a part of the rays forming F_2 are shown. Light appears to come from two virtual sources S_1 and S_2, each distance $D_1 + D_2$ from observer; $S_1 S_2 = d$. The distance from F to S_1 (reflected ray extended) is made equal to $D_1 + D_2$. The angle between reflected rays is twice the angle between the mirrors.

Because D_2 is small, $\sin 2\alpha \approx \frac{d}{D_1+D_2} \approx \frac{d}{D_1} \approx 2\alpha$

The path difference $SF_1 - SF_2 = \lambda$ for constructive interference.

The triangles S_1S_20 and $F_1F_2S_1$ are approx. similar;

therefore $\frac{\lambda}{d} = \frac{e}{D_1+D_2}$ and $\lambda = \frac{2\alpha e D_1}{D_1 + D_2}$

All the quantities on the right side are measurable. Fresnel Computed the probable wave lengths of red light to be about 40,000 per inch, and violet, about 80,000 to the inch.

In another experiment, Fresnel demonstrated that in the center of the shadow of a small circular (or spherical) object, placed very far from the source of light, there was a bright spot of light. A wave could bend around an obstacle and appear again as light within a region of shadow.

Fresnel also gave the first mathematical treatment of the theory of transverse wave motion. With it he was able to account for double refraction in crystals, for the first time. This work he did in the eighteen-twenties.

The next important contribution that had an important bearing on the nature of light was the measurement of the velocity of light. Romer, in 1676, found that it was finite, from his observations of the periodic eclipses of one of the

7 RM is a large distance (several kilometers) as compared to SR; and S_1M_2 is large compared to S_1S_1'.

Suppose the mirror R has rotated through an angle $\underline{\Phi}$. Then the returning rays at R are displaced by an angle $2\underline{\Phi}$ at R. $\underline{\Phi}$ is a very small angle. ~~Therefore angle $S_1M_2S_1'$ equals $\underline{\Phi}$, if LR and M_2L are approximately equal.~~

Then $\sin\Phi \approx \tan\Phi \approx \frac{S_1S_1'}{S_1R}$ gives the angle of rotation of R..

R is rotating at a constant known rate of n rotations per second. Then $\frac{\Phi}{t} = 2\pi \frac{\text{radians}}{\text{rot.}} \cdot n \frac{\text{rot.}}{\text{sec}}$

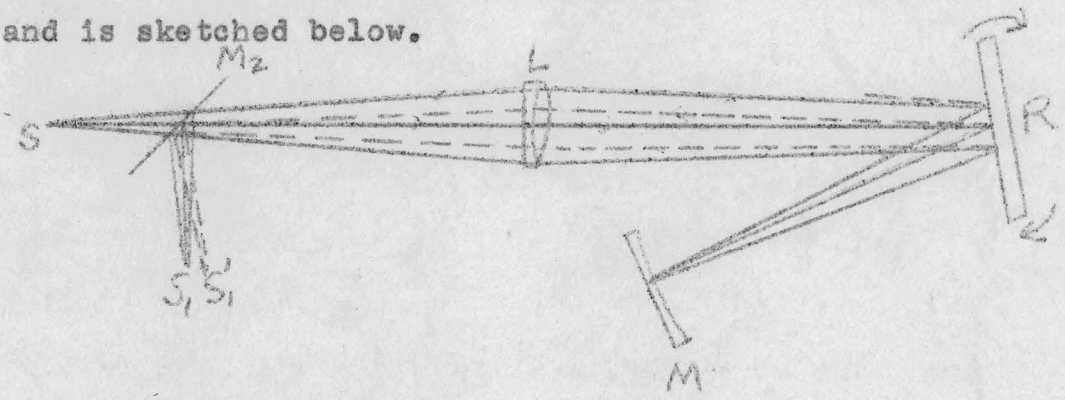
And $t = \frac{\Phi}{2\pi n}$ is the time for the rotation $\underline{\Phi}$ that corresponds to the displacement S_1S_1'.

The speed of light c is then computed as follows.

$$c = \frac{\text{dist.}}{\text{Time}} = 2\overline{RM} \cdot \frac{2\pi n}{\Phi}$$

$$c = \frac{4\pi n \cdot \overline{RM}}{\Phi} \quad \frac{m.}{\text{Sec.}}$$

satellites of Jupiter. As the earth moved farther away from Jupiter, the period of the satellite appeared to increase. The observation was accounted for by assuming that the light had farther to travel than before. The size of the earth's orbit was not too well-known and the velocity of light determination was not too reliable. Fizeau made the earliest terrestrial determination of the speed of light. His apparatus was modified by Foucault and is sketched below.



A source of light S sends light through a plate of glass M_2, through a converging lens L, off a rotating mirror R, and to a concave mirror M. The light returns to R (now slightly rotated) and retraces a path to M_2. There, part of it is reflected to the observer at S_1 (or S_1'). R is turning at high speed as the light passes from R to M and back. The returning beam is displaced from S_1 to S_1'. The distance S_1S_1' is measured and used to find the angle through which R turned.[7] Knowing the angular speed of R and the distance RM, it is possible to compute c, the

velocity of light. Foucault found the speed of light to be 298,600 km./sec. He introduced a tube of water into the light path and determined that the speed of light in water was considerably less. The wave theory of light was on firm ground. We recall the fact that a mechanical corpuscle of light would necessarily travel faster in water than in air. Foucault had finally given the answer about 1850.

The foundation laws of electricity and magnetism were discovered during the last half of the eighteenth and through the nineteenth century. In about 1785 Coulomb developed the torsion balance and used it to show that electrostatic forces varied as the inverse square of distance. Before 1800, Volta produced the first steady currents from a "pile" of zinc and copper plates separated by brine-soaked paper. Oersted made the opening discovery of the relation of magnetism and electricity. A pivoted magnetic needle aligned itself at right angles to a current of electricity. Ampere showed quantitatively the action of a magnetic field on a current. Faraday's many discoveries included: the electric motor principle; the law of electromagnetic induction (a changing current in one wire could cause a current in another wire nearby); Faraday's laws of electrolysis; in 1840 the conservation of energy; the "Faraday effect" in light (the plane of polarization of light may be changed by a strong magnetic field). Gauss' law of electric flux became known: that the net number of lines of electric force

Crossing a closed surface in an outward direction equals the net positive charge enclosed within the surface. All the essentials of the laws of electricity and magnetism were generalized in the mathematics of James Clerk Maxwell in 1856. These four equations express the laws.

$$\text{Curl}\,\vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad \text{div}\,\vec{B} = 0$$

$$\text{Curl}\,\vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \qquad \text{div}\,\vec{D} = \rho$$

E is the electric field; D is called electric displacement; p and J are the charge density and current density, respectively; B is the magnetic flux density and H is the magnetic field vector. In empty space, the following conditions hold.

$$\vec{D} = \epsilon_0 \vec{E} \qquad \vec{B} = \mu_0 \vec{H} \qquad \vec{J} = 0$$

The first vector equation is a statement of Faraday's law of magnetic induction, "the induced emf in a moving conductor equals the magnetic flux density experienced by that conductor". The second vector equation states the Ampere law, "The tangential component of the magnetic field at any point on a closed curve is proportional to the net current flowing through the area within the curve". One of the scalar equations is a statement of Gauss' law given above. The other scalar equation is equivalent to saying that a magnetic pole cannot be isolated. If one takes the Magnitude of E, or of the electric charge, and writes its value in electromagnetic units, divided by its

value in electrostatic units, the constant is significant. Maxwell showed that the velocity of propogation of waves in space should equal this ratio, if such waves were produced by oscillating electric charges. The value of the constant proved to be within three percent of the velocity of light then known. Maxwell suggested that light might consist of electromagnetic waves.

The existence of Maxwell's electromagnetic waves was confirmed by Hertz in 1887. He found that an oscillating circuit with a spark gap produced waves in space. The waves were detected by a second oscillating circuit separated in space from the first and tuned to it. A spark in the receiver circuit indicated the passage of the waves through space. But something else of great importance came out of Hertz' experiment. The receiver spark gap was inclosed in a box to facilitate observation. Inside the box the gap had to be made shorter to detect the same waves. Hertz hypothesized correctly that the ultraviolet light from the transmitter spark influenced somehow the spark emission in the receiver. He had discovered the photoelectric effect.

A year later, Hallwachs charged a plate of polished zinc negatively. An electroscope showed that ultraviolet light from an arc caused the zinc plate to lose charge. A positively charged plate was found to experience no effect. Hallwachs used a more sensitive electrometer and

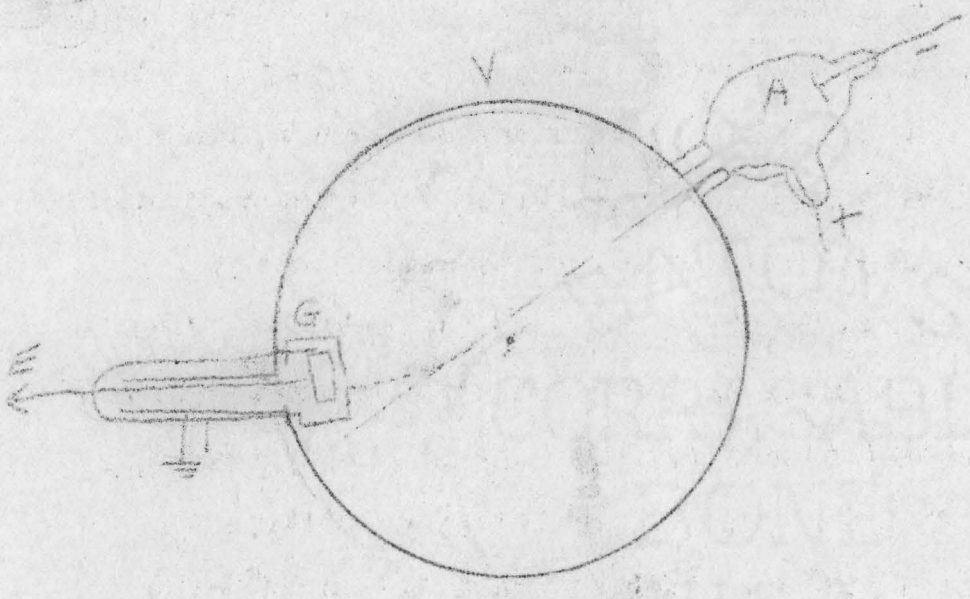


Figure 2. (Modified) Perrins Apparatus

The cathode A is the source of the rays, which are then focused by the narrow hole in the anode (+). Normally, the cathode rays follow the straight path. But Helmholtz coils make a magnetic field perpendicular to the plane of the paper. With the field on, the rays pass through the hole in the metal cylinder C and onto the electrometer connected to E. Thus, a much higher electrometer reading with the field on indicated that the rays were behaving as negatively charged particles.

found that even a neutral plate would acquire a small positive charge due to the light (i.e., there was again a loss of negative charge). Stoletow connected a photoelectric (polished zinc) plate to the negative side of a high-voltage battery. A grid was connected through a sensitive electrometer to the positive side of the battery. When ultraviolet light fell on the plate, a continuous (photoelectric) current flowed from the plate, through space, and through the electrometer, back to the battery.

Lenard, by investigations carried out in 1889, determined that the charges lost in the phenomenon of the photoelectiic effect were similar to the well-known cathode rays. Application of a magnetic field showed that photoelectric rays were deflected in the same way as were cathode rays. At that time, the exact nature of the cathode rays themselves was not known. The next development was a series of experiments that converged toward the discovery of the electron.

In 1895 Perrin succeeded in showing by electrometer measurements that the cathode rays in a Crooke's tube were negatively charged. Meanwhile, Lenard found by direct measurement that the photoelectric radiations were negatively charged. He believed, however, that they were pure negative electricity, apart from matter.

In 1897 J. J. Thomson began experiments which enabled him to know more about the nature of cathode rays. The

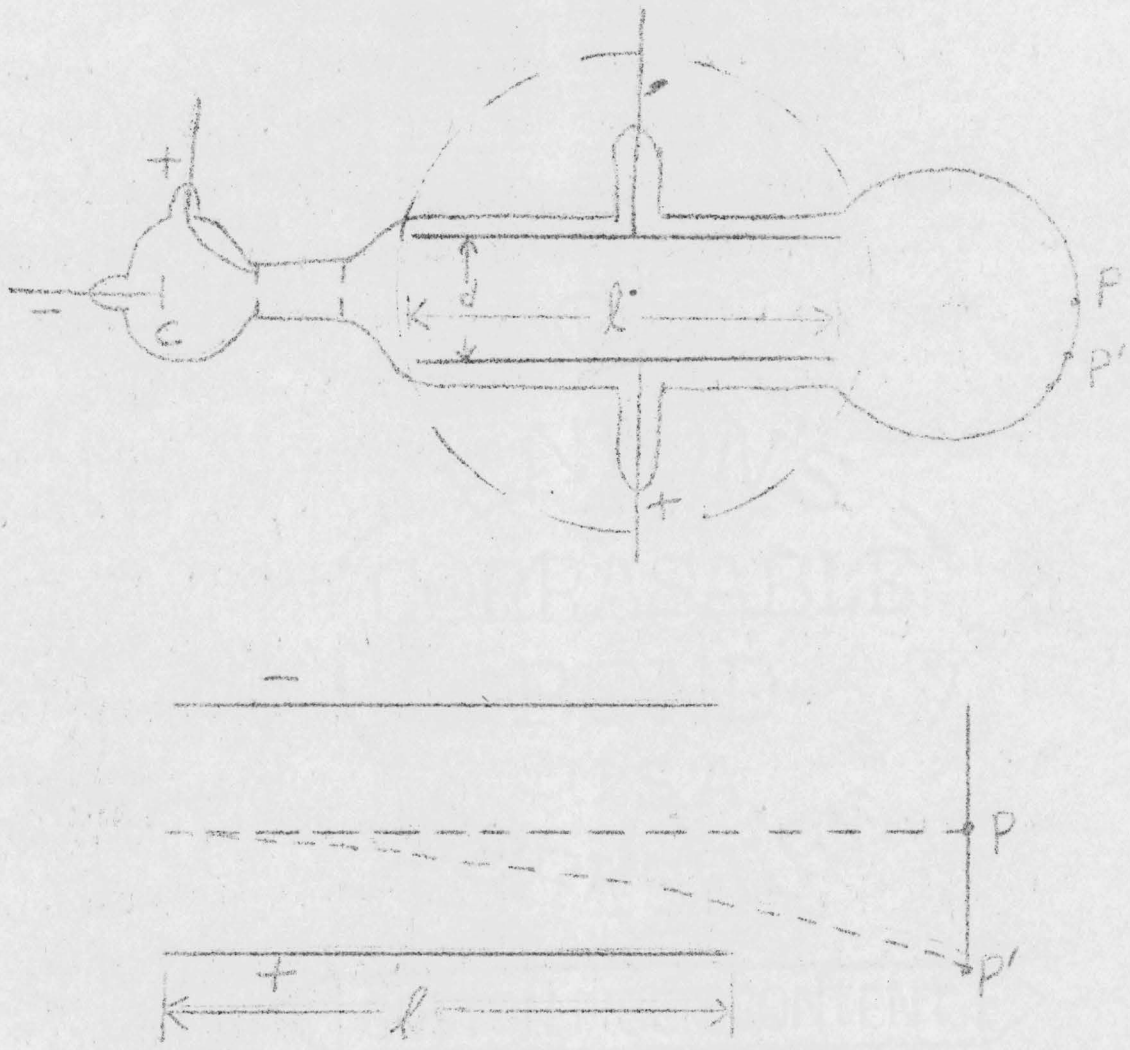


Figure 3.
Thomson's Apparatus

8 The charged particles are acted upon by a constant force in the y-direction while between the plates. Then the path between the plates is parabolic. The path after leaving the plates is a straight line. For "cathode ray" velocities, the curvature is very slight. Therefore, we will approximate by saying, represent the whole path by a straight line.

Since y and b are parallel, the proportion

$\frac{y}{b} = \frac{l}{x}$ holds, for the similar triangles formed.

rays were emitted at high speed inside a highly evacuated tube. A hole in the anode allowed the beam to continue at constant speed between two parallel plates. The metal plates could be charged electrically. A pair of Helmholtz coils were arranged outside the tube so as to produce a magnetic field at right angles to the electric field of the plates. The cathode rays could then be deflected in the same plane by the two fields. The end of the tube opposite the cathode was made fluorescent so that one could detect the beam's position. A spot appeared on the end of the tube and this spot was deflected by the electric field. Then, by increasing the current in the coils, the magnetic field was applied. The field was increased until the beam came back to its undeflected position. If the plate separation is d, the applied plate potential is V, the magnetic field is B, and the rays are charged particles of velocity v and charge q on each, then: $Eq = Bqv$ ($\frac{v}{d} = E$, the electric field) and the equation states the balanced deflecting forces of the two fields. The equation enabled Thomson to find the velocity of the rays. Then the magnetic field was turned off. The electric deflection b was measured. b is proportional to y, the deflection during passage between the plates. If l is the length of the plates and x is the distance from the beginning of the plates to the screen, then $\frac{y}{b} = \frac{l}{x}$ or $y = \frac{bl}{x}$. The deflection y is related to the acceleration as follows:

$$y = \tfrac{1}{2} a t^2 = \tfrac{1}{2} \frac{F}{m} t^2 \quad \text{where } t = \frac{l}{v}$$

$$y = \tfrac{1}{2} \frac{E e}{m} \left(\frac{l}{v}\right)^2; \quad \frac{e}{m} = \frac{2y}{E} \frac{v^2}{l^2} = \frac{2b}{dlx} \frac{V}{B^2}$$

From the last equation, the charge-to-mass ratio, a basic property of the particle is computed. The value obtained by Thomson was 1.7×10^7 e.m.u. Cathode rays behaved as negatively-charged masses in motion. Further work by Thomson revealed that these masses were not peculiar to cathode rays but were also found in other types of emission.

> The value of e/m has been determined in this way for the negatively electrified particles which form the cathode rays which are so conspicuous a part of the electrical discharge through a gas at low pressures; and also for the negatively electrified particles emitted by metals (1) when exposed to ultra-violet light, (2) when raised to the temperature of incandescence. ... the value of e/m is the same whatever the nature of the gas in which the particle may be found, or whatever the nature of the metal ... 2

The value of e/m was about 1700 times the charge-to-mass ratio of hydrogen ions. The ratio for hydrogen ions had been found by methods of electrolysis. The question was, is it due to a greater charge or a smaller mass that e/m for cathode rays is so large. The answer came after the electric charge was determined.

While Thomson was investigating the nature of the

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[2] J. J. Thomson, Electricity and Matter (New York, 1904), p. 86.

[9] Townsend, who did a similar experiment, collected the water vapor and weighed it. Thomson computed the weight of the cloud from theoretical consideration of the amount of cooling produced by the expansion. He used the known differences between the densities of saturated water vapor at room temperature and at the cooler temperature. Here, we will not use the exact method of computation used by Thomson, but the results are similar.

Let q be the heat per unit mass liberated per change in temperature ΔT; let r be the heat of vaporization (heat liberated per unit mass of vapor that condenses); let A be the reciprocal of the mechanical equivalent of heat; let u be the change in volume and p the pressure; let m be the mass of water vapor condensed and m' the mass of all the vapor in the chamber.

The work done on expansion is p x u, and the total heat liberated is A p u. Then $m'r + mq = Apu$, or $m' = \frac{Apu - mq}{r}$. The quantities on the right are either measured or found from tables (pp. 2046, 2047 of CRC Handbook, 33rd ed.) and the mass of vapor in the cloud trail can be found.

cathode rays, C. T. R. Wilson invented the cloud chamber. This device could detect the presence of a charged particle. Water vapor in the saturated air in the chamber would condense along the path of charged particles more easily than along the path of uncharged particles. The condensations appeared in the form of a cloud trail. Soon Thomson made use of the cloud chamber to investigate the charge on the cathode rays. He used a piece of radium inside the chamber to produce the ionized particles. Then he observed the rate of fall of the cloud trails. An Electrometer element inside the chamber collected the charge from the particles. The total amount of vapor in a cloud could be computed from the pressure and temperature.[9] If the radius of an average drop were known, then the number of drops could be found. Thomson used the empirical law of Stokes to compute the radius: $a = \sqrt{\frac{9}{2}\frac{\eta}{\rho g} v}$ v is the rate of fall; p the density of the drops; n the viscosity of the medium; g the acceleration due to gravity; a represents the radius. Each drop was assumed to have one unit of charge. The total charge on the electrometer was divided by the number of ions. Thomson obtained a value of 3.1×10^{-10} e.s.u., which turned out to be about one third too small. But it was clear that the cathode rays (electrons) were much smaller in mass than hydrogen ions.

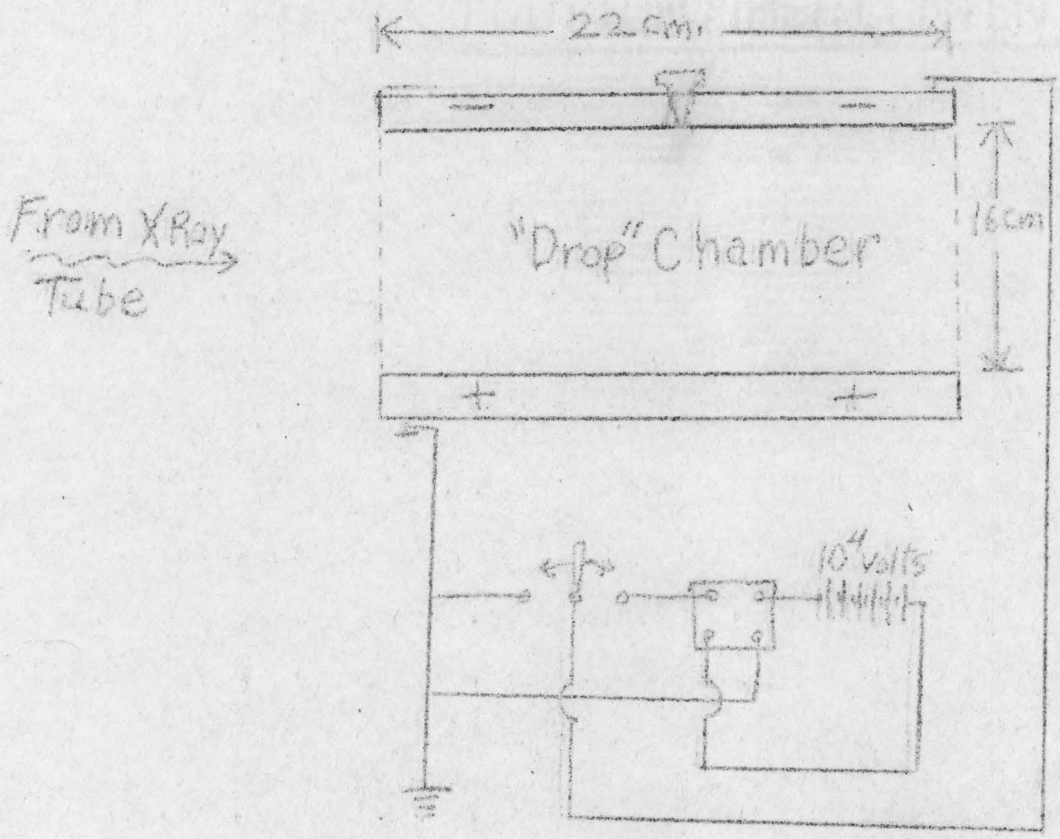

Figure 4.

Millikan's Oil-Drop Apparatus

R. A. Millikan accurately determined the value of e. He began by trying to eliminate some of the uncertainties in the Thomson method. The uncertainties included the unknown rate of evaporation of the drops during the fall. While studying the evaporation effects, Millikan made two important discoveries.[3] First, he found that with a strong electric field, he could hold individual drops in view for nearly as long as a minute. Second, some of the drops picked up ions and changed velocity as he observed them. This suggested to him that one could determine the charge on captured ions by observing drops before and after a capture. The expansion chamber was given up in favor of different apparatus. A small chamber was made of two metal plates (22 cm. in diameter and 16 mm. apart) for the top and bottom. The plates were connected to a 10,000-volt battery. Oil was sprayed into an upper chamber above the plates. A few of the drops came down between the charged plates through a small hole in the upper plate. Individual drops were observed through a telescope equipped with parallel horizontal cross-hairs.

From the rate of fall of an uncharged drop, Millikan found the radius and weight. A sphere of radius a moving at speed v_o through a fluid of viscosity n encounters a force of resistance $6\pi nav_o$. The weight of the droplet

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[3] R. A. Millikan, Electrons (+ and -) (Chicago, 1935) pp. 64, 65.

is $\frac{4}{3}\pi a^3 \rho g$, where p is the density of the oil. At the terminal velocity then $\frac{4}{3}\pi a^3 \rho g = 6\pi\eta a v_0$ enabled Millikan to determine a and thus the weight of the drop. If the drop then picks up charge e and is in an electric field E, then the additional force on the drop is eE. So $eE + \frac{4}{3}\pi a^3 \rho g = 6\pi\eta a v_1$. The drop falls now with speed v_1.

The relation $eE = 6\pi\eta a(v_1 - v_0)$ makes it possible to compute, from the other known quantities, the value of e. After observing velocities on thousands of drops, Millikan knew that the velocity differences (as $v_1 - v_0$) could all be expressed as some multiple of a smallest number. The drops never changed velocities fractional amounts of that number. That meant that e was never smaller than some unit of charge and never occurred but in multiples of that unit--the electron charge was quantized. Thomson and others had <u>assumed</u> a unit of charge in their work. Millikan <u>found</u> one in his. Whether the speed of a drop changed as a result of an uncharged drop acquiring some charge, or as a result of a charged drop gaining or losing some charge, the result was the same--a fundamental unit of charge. It is also noteworthy that Millikan did not assume Stokes' law of fall--he checked it and corrected its predictions slightly. Millikan obtained a value of e in 1910. His most reliable determination was in 1913, a value which was not improved upon for twenty years. He found

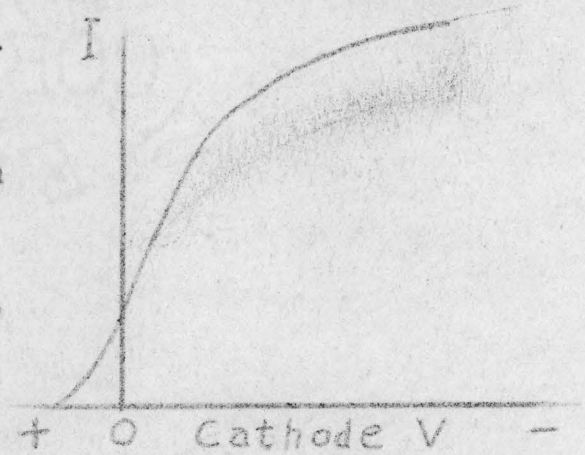
10 The following is a sample computation, from some of the early data of Millikan, and using the form of the equation found on page 15. A drop had been observed falling with no electric field, with a velocity v_o. It had also been observed with several other different speeds, v_1, different for each number of charges on the drop. The velocities all differed by multiples of .0088 cm/sec. This particular drop had three units of charge on it. By Stokes' law, the radius $a = 3.1 \times 10^{-4}$ was determined.(cm.) The viscosity $n = 1.82 \times 10^{-4}$ dyne sec/cm.^{2}/ and the field was 6×10^3 volts/cm. $= 6 \times 10^3 / 3 \times 10^2 = 20$ statvolts. The computation (with $v_1 - v_o$ corrected for number of charges) is as follows.

$$e = \frac{6 \times 3.14 \times 1.82 \times 10^{-4} \frac{\text{dyne sec}}{\text{cm}^2} \times 3.1 \times 10^{-4} \text{cm} \times 8.8 \times 10^{-3} \frac{\text{cm}}{\text{sec}}}{20 \text{ esu/cm}}$$

$$e = 4.7 \times 10^{-10} \text{ esu.}$$

$e = 4.807 \times 10^{-10}$ e.s.u., with a possible error of 5 in the last figure. Millikan's determination of e made it clear that the negative rays (now called electrons) were small particles with the same quantity of charge as hydrogen ions.

Lenard continued his work on the photoelectric effect. He put the emitter and another element (anode) in an evacuated tube. The anode was made neutral and the emitter (cathode) subjected to a varying potential. An electrometer connected to the anode measured the photoelectric current. Lenard plotted the current as a function of the cathode potential. Even when the cathode was somewhat positive, ultraviolet light could liberate some electrons. There was an increase of current as the cathode became less positive, until a maximum current was reached. Photoelectric rays then had a certain energy to start with--enough to overcome the positive voltage. The most energetic photoelectrons (with maximum velocity) would have kinetic energy given by $\frac{1}{2} m v_{max.}^2 = V_0 e$. Further experiments showed that the current increased in proportion to the intensity of light, but the fastest electrons were liberated no matter how low the intensity of light on the cathode. That is, V_0 was the same no matter how far away the light source



is from the cathode. The fact that more electrons were freed from the metal at smaller retarding potentials must mean that there are electrons with many different energies. Lower energy electrons were accounted for by the view that some electrons were deeper in the metal and used up quite a lot of energy in getting to the surface. Some electrons were deep enough that an accelerating (negative) voltage was required to assist the light in setting them free. Lenard believed that a kind of explosive force in the atom was released by the light. Light, he reasoned, was only a trigger and a stronger trigger only released a certain atomic force on the electron. Einstein attributed the electron's energy to the light itself. His explanation of the photoelectric effect was based on his theory of the nature of light, a quantum theory. The theory is built on Planck's theoretical work. We will interrupt our account of the progress of the knowledge of the photoelectric effect to summarize Planck's contributions on the nature of radiation emitted from black-bodies.

Black-bodies are those objects that absorb all the radiant energy of all wave-lengths that is incident on them. Such a body is also able to emit all wave-lengths of energy. W. Wien's distribution law for radiation from black-bodies related the energy emitted E to the temperature T and the wave-length λ. $E_\lambda = \frac{c_1}{\lambda^5 e^{c_2/\lambda T}}$ Experiment verified the relation for small wave-lengths and temperatures. But Wien's formula did not hold for

long wave-lengths. Rayleigh later showed that $E_\lambda = K\frac{T}{\lambda^4}$ for the longer wave-lengths. Planck intended to account for all the experimental facts of radiation by a single radiation law. This work he did in 1900.

Planck began by assuming that the radiated energy could be represented by the energy of simple oscillators. He used the concept of entropy S in terms of the energy E and temperauure T: $dS = \frac{dE}{T}$ This expression was differentiated. The derivatives of the energy expressions of Wien and Rayleigh were separately substituted into the second order differential equation, obtaining [11] two expressions: $\frac{1}{\frac{d^2S}{dE^2}} = -BE$ and $\frac{1}{\frac{d^2S}{dE^2}} = -\frac{E^2}{C}$.

Then Planck assumed that $\frac{1}{\frac{d^2S}{dE^2}} = -BE - \frac{E^2}{C}$.

The solution of the above differential equation was expressed as $\frac{dS}{dE} = \frac{1}{B}\log\left(1+\frac{BC}{E}\right)$. By definition of entropy, 1/T was substituted for dS/dE, and the final result was $\frac{1}{T} = \frac{1}{B}\log\left(1+\frac{BC}{E}\right)$. The energy of the oscillator was found to be of the form $U = \frac{BC}{e^{B/T}-1}$. Then the energy of the radiation can be written as $E_\lambda = \frac{A}{\lambda^5}\cdot\frac{1}{e^{B'/\lambda T}-1}$ where B in the oscillator equation is proportional to $\frac{1}{\lambda}$ and c is proportional to $\frac{1}{\lambda^4}$. A and B' in the radiation equation are constants. For small values of λT the -1 term can be dropped. So $E_\lambda = \frac{A}{\lambda^5}\cdot\frac{1}{e^{B'/\lambda T}}$ (Wien's law). If λT is large, then the series $e^{B'/\lambda T} = 1 + \frac{B'}{\lambda T} + \cdots$

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[11] See appendix.

reduces to approximately $1 + \frac{B'}{\lambda T}$. This means the energy $E_\lambda = \frac{A}{B} \cdot \frac{T}{\lambda^4}$ (Rayleigh's Law). Thus Planck had fitted together the experimentally correct laws of radiation. He did not stop with that. He wished to derive the radiation law from the physical principles of radiation.

Planck started again with entropy. Boltzmann had found that S = k log W, where W is the probability that a system is in a certain state. Planck wished to find the probability of any particular distribution of the total energy U of a system, among many oscillators that comprise the system. If the energy were divided into infinitesimal amounts, then there was no answer to the probability. He assumed that the energy was distributed among the oscillators in multiples of a finite amount e. Suppose P units of energy are divided among N oscillators; then U = Pe. The average energy of a single oscillator is given by $\bar{U}$ = Pe/N. Planck used for W the expression in N and P for large N. In the entropy equation he then substituted $\bar{U}$ N/e for P to obtain the entropy for a single oscillator. S was then an expression in $\bar{U}$ and e. The definition and Wien's displacement law λT = constant, gave $\frac{dS}{d\bar{U}} = \frac{\lambda}{\text{Const.}}$ or, in terms of frequency, $\frac{dS}{d\bar{U}} = \frac{c}{\nu \cdot \text{Const.}}$ Then S is entirely given in terms of $\bar{U}$, v, and constants. Planck then let e = hv be one of the constants. The solution of the resulting differential equation in S is $\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1}$. When Planck converted the energy of

the oscillator to the energy of the radiation, he finally obtained $E = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{ch/k\lambda T} - 1}$ which agrees with his earlier results if A = 8 Π c h and B' = c h/k. Thus it was by the necessary assumption that radiation is emitted in discrete amounts hv that Planck obtained an energy radiation formula that fitted the best experimental results. This discontinuous picture of light would not fit into classical electromagnetic theory. The uses of Planck's constant h by other physicists in successfully explaining so many phenomena have indicated that the "quantum of action" is a fundamental physical quantity.

Einstein accounted for the photoelectric effect by using Planck's ideas. Einstein assumed that the exciting light was quantized in units of hv. These quanta penetrate the surface of a metal and encounter electrons, he said. Part or all of a quantum might be given to an electron, but Einstein assumed that all of it was given. The energy became kinetic energy for the electron. Some of the energy was used up in getting to the surface of the metal. The remaining kinetic energy of the electron was expressed as $\frac{1}{2}mv^2 = h\nu - P$. P is the work function, the amount of energy required to free the electron. The equation showed that the photoelectron energy was independent of the intensity of the light, in agreement with experiment. If a retarding (positive) potential were applied to the metal, a potential just large enough to

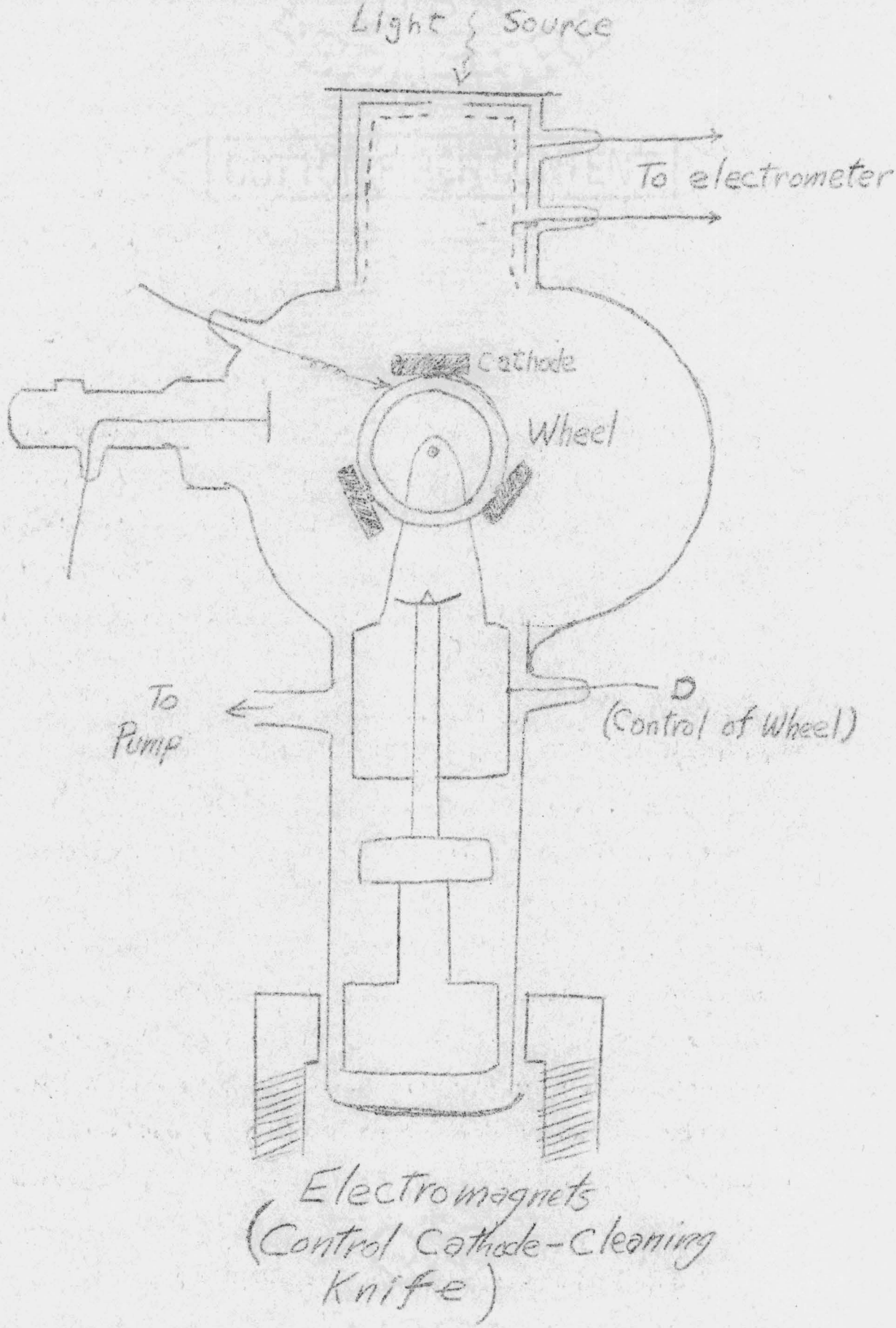

Figure 5.

Millikan's "machine shop in vacuo"

stop all the electrons from escaping, then $V_o e = h\nu - P$. The last equation predicted that, for any given metal, the retarding potential ought to be proportional to the frequency of the incident light. So it was in 1905.

Millikan confirmed the prediction by experiment. He found it necessary to work with the alkali metals because they responded to the whole range of visible and ultraviolet light in emitting photoelectrons. Using his "machine shop in vacuo", Millikan found that different frequencies did require different stopping potentials. From the plot of $V_o e$ against frequency, he demonstrated that: the energy of the fastest electrons is proportional to the frequency of the light; the slope of the line is h, whatever the metal; the threshold frequency ν_o is a property of the metal used as the emitter.[4] $V_o e = \frac{1}{2} m v^2_{max.} = h\nu - h\nu_o$ where $h\nu_o = P$, the Einstein work function. The average value of h obtained in this way by Millikan was 6.56×10^{-27} erg-sec. Planck, Einstein and Millikan had established that radiant energy can behave as quanta.

Those quantum discoveries dealt with radiations from infrared to ultraviolet. In 1923, A. H. Compton found

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[4] R. A. Millikan, op. cit., pp. 239-243.

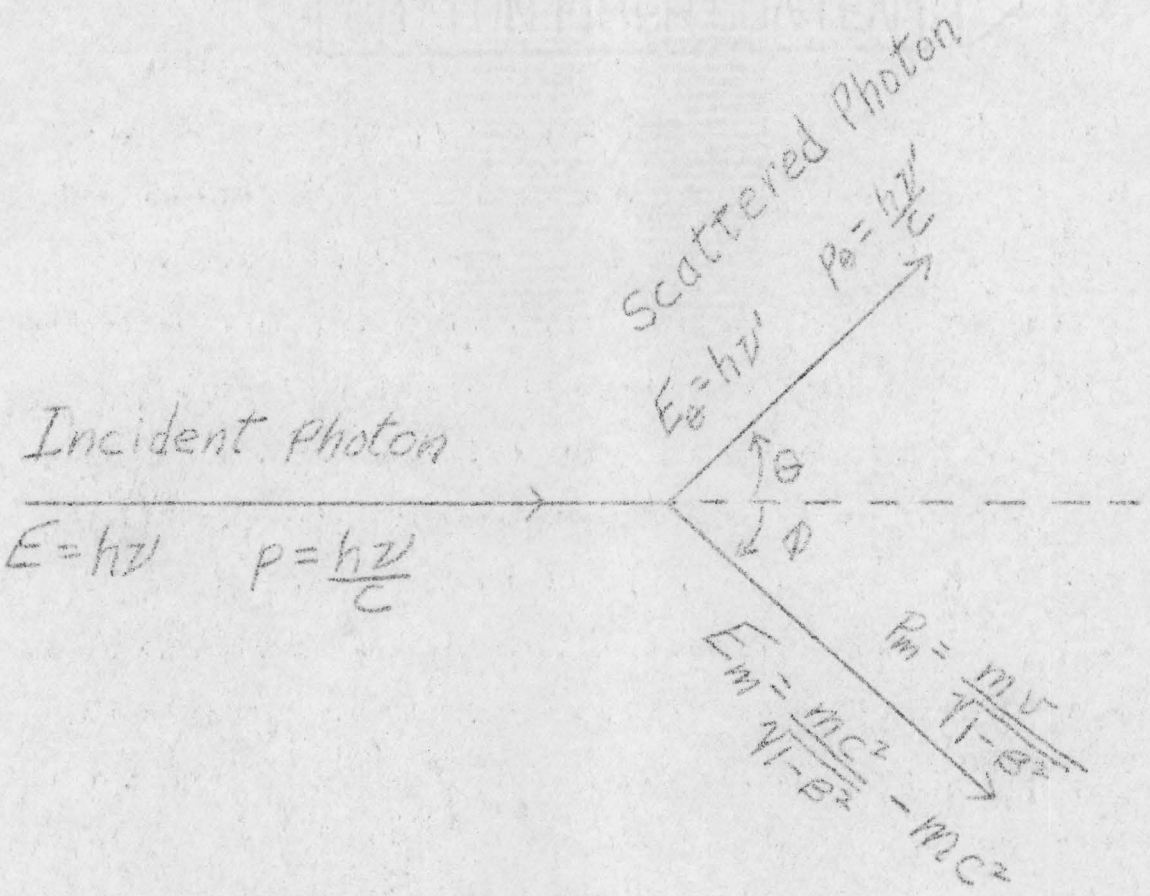

Figure 6.

Vector diagram, Compton Effect

that X rays also must exist as quanta. He found that some X rays were scattered by being glanced off graphite crystals. The scattered radiation was found to be of longer wave-length than the incident rays. The phenomenon was different from fluorescence. The scattered rays were independent of the scatterer; they were dependent on the wavelength of the incident beam and very nearly equal in wavelength. Furthermore, the new radiations were polarized, unlike fluorescent rays.[5] Compton accounted for the new phenomenon by first assuming X rays to be quanta as had Einstein assumed ultraviolet quanta. Let a quantum of energy collide with an electron in the crystal. From the collision the electron acquired a velocity v. For the electron, the kinetic energy is $T = \frac{mc^2}{\sqrt{1-v^2/c^2}} - mc^2$ (m is the rest mass of the electron). By the conservation of energy, $h\nu = h\nu' + \frac{mc^2}{\sqrt{1-v^2/c^2}} - mc^2$ where ν' is the frequency of the scattered radiation. By the conservation of momentum, considering the x and y components independently, come the two equations:

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\theta + \frac{mv}{\sqrt{1-v^2/c^2}}\cos\phi$$

$$0 = \frac{h\nu'}{c}\sin\theta - \frac{mv}{\sqrt{1-v^2/c^2}}\sin\phi$$

Squaring both momentum equations and adding the results,[12] the result is $\nu - \nu' = \frac{h\nu\nu'}{mc^2}(1-\cos\theta)$ or $\lambda' - \lambda = \frac{h}{mc}(1-\cos\theta)$,

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[5] A. H. Compton, X Rays and Electrons (Princeton, 1926) pp. 11-14, 70.

12 Using the form of the momentum and energy equations where $\beta = v/c$:

Energy equation $h\nu_0 = h\nu_\theta + mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right)$ (a)

Momentum $\frac{h\nu_0}{c} = \frac{h\nu_\theta}{c}\cos\theta + \frac{m\beta c}{\sqrt{1-\beta^2}}\cos\Phi$ (b)

$$0 = \frac{h\nu_\theta}{c}\sin\theta + \frac{m\beta c}{\sqrt{1-\beta^2}}\sin\Phi \quad (c)$$

Then make the following substitutions: $M_0 = \frac{h\nu_0}{mc^2}$; $M_\theta = \frac{h\nu_\theta}{mc^2}$

Divide (a) by mc^2: $M_0 - M_\theta = \frac{1}{\sqrt{1-\beta^2}} - 1$ (a')

Divide (b) by mc: $M_0 - M_\theta\cos\theta = \frac{\beta}{\sqrt{1-\beta^2}}\cos\Phi$ (b')

Divide (c) by mc: $M_\theta\sin\theta = -\frac{\beta}{\sqrt{1-\beta^2}}\sin\Phi$ (c')

Square (a'): $M_0^2 + M_\theta^2 - 2M_0M_\theta + \frac{2}{\sqrt{1-\beta^2}} = \frac{1}{1-\beta^2} + 1$ (a'')

Square (b'): $M_0^2 + M_\theta^2\cos^2\theta - 2M_0M_\theta\cos\theta = \frac{\beta^2}{1-\beta^2}\cos^2\Phi$

Square (c'): $M_\theta^2\sin^2\theta = -\frac{\beta^2}{1-\beta^2}\sin^2\Phi$

Add the last two: $M_0^2 + M_\theta^2 - 2M_0M_\theta\cos\theta = \frac{\beta^2}{1-\beta^2}$ (d)

Subtract (d) from (a''):

$$-2\left[M_0M_\theta(1-\cos\theta) - \frac{1}{\sqrt{1-\beta^2}}\right] = \frac{1-\beta^2}{1-\beta^2} + 1 = 2$$

But, from (a'): $M_0M_\theta(1-\cos\theta) = M_0 - M_\theta$

Then $\frac{1}{M_\theta} - \frac{1}{M_0} = 1 - \cos\theta$

and, since $\frac{1}{M_\theta} = \frac{mc\lambda_\theta}{h}$ and $\frac{1}{M_0} = \frac{mc\lambda_0}{h}$

therefore

$$\lambda_\theta - \lambda_0 = \frac{h}{mc}(1-\cos\theta)$$

after combining the sum with the energy equation. Experimentally, Compton had found that $\lambda - \lambda' = .024(1 - \cos\theta)$. So a quantum theory for X rays gave results in agreement with experiment. The recoil electrons Compton predicted were later detected in a cloud chamber. The classical theory could not account for the increased wave-length. An electromagnetic wave incident upon a charged particle would vibrate it at the wave's own frequency. Any light emitted from the atomic particle would be of the same frequency, no matter what the direction of the secondary radiation.

Let us turn now to another matter--the structure of matter. J. J. Thomson suggested in about 1900 that the atom was a shell of positive charges with negative electrons interspersed.[13] That atomic model was based on his work with positive and negative ions and electrons in vacuum tubes and magnetic fields. Rutherford in 1911 found that alpha particles bombarding a layer of gas were sometimes deflected through large angles. This was just what should occur if the atoms had a condensed mass of positive charge. For Rutherford knew the charge and mass of the particles. The cloud chamber tracks of the alpha particles could not be explained by a hollow atom. Rutherford's theory of the atom gave it a nucleus, positive with a large mass and electrons surrounding the nucleus at a large distance compared to the nuclear radius.

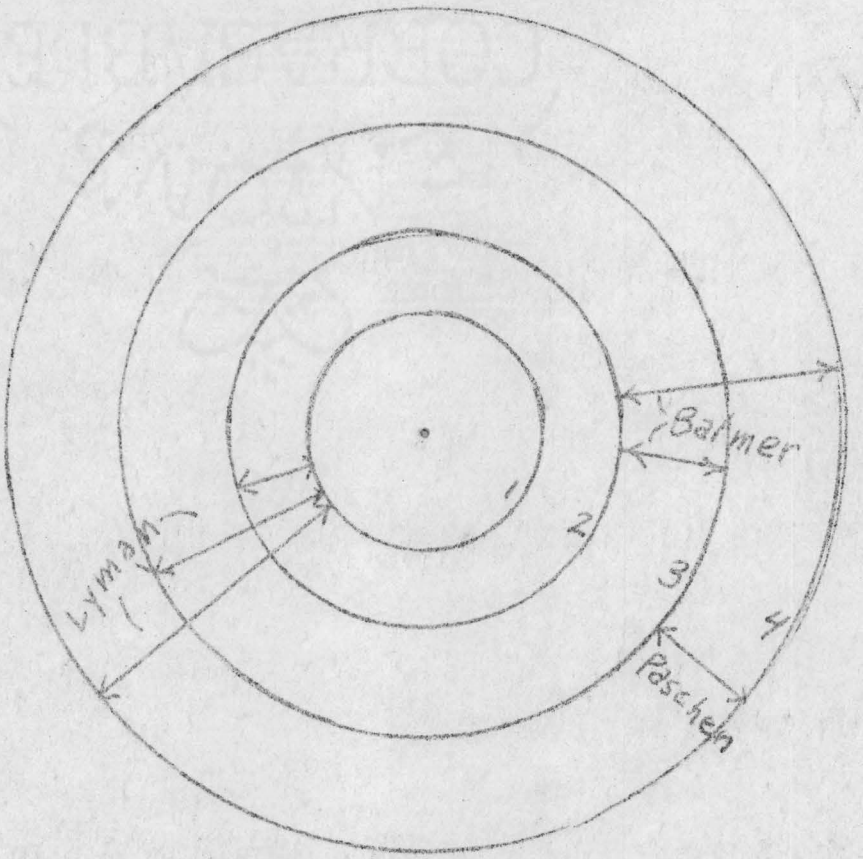
13 It is more accurate to say that the Thomson atom was a sphere of uniformly distributed + charge with electrons embedded.

Niels Bohr was working under Rutherford in 1913 when Bohr developed his own theory of the atom. He began with a model of the hydrogen atom. In our discussion we will start with hydrogen, too. The theory (approx.) may be extended to hydrogen-like atoms--atoms with not too complex an outer electron structure, or partly-ionized atoms. Bohr built his theory to agree with the evidence at hand from the line spectra of incandescent gases, especially hydrogen. Rydberg had showed in 1890 that the wave number (reciprocal of wave-length) and the number of position in a series of spectral lines were in the relation $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{m^2}\right)$. This equation is based on the Balmer series of hydrogen, a series of spectral lines in the visible region. The m must be an integer greater than 2. W. Ritz generalized the formula in the "combination principle". According to the principle, the wave number of every spectral line can be expressed as the difference of two terms. These terms for hydrogen have the form R/m^2. $\frac{1}{\lambda_1} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$ and $\frac{1}{\lambda_2} = R\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$ give the wave numbers for two of the Balmer lines. Further, the principle predicted that $R\left(\frac{1}{3^2} - \frac{1}{4^2}\right)$ might exist. Paschen later found this line as part of a series in the infrared region of the hydrogen spectrum. Bohr's atom agrees with the Ritz rule.

An atom of the kind proposed by Rutherford could not long exist by classical laws. The positive nucleus

and the electrons could not remain stationary. If one moved with respect to the other, continuous radiation should emanate from the atom; it would lose all its energy and collapse. Bohr postulated a planetary atom model that obeyed classical laws <u>except</u> that it could exist in a state of non-radiation. Secondly, radiations could occur only when the electron made a transition from one stationary state to another. Third, the radiation would be equivalent to that given off by a harmonic oscillator of constant frequency. This frequency had no simple relation to the electron's motion. As a result of these postulates, Bohr showed that $h\nu = E_2 - E_1$ where E_2 and E_1 are the stationary-state energies of the electron, and h is the Planck's constant. Thus the frequency of the radiation, ν is the difference of two terms. There is agreement with both the Einstein theory of radiation and the Ritz principle of spectral lines. The following discussion will show how the agreement may be arrived at.

Bohr's stationary states were determined by the condition that the angular momentum of the orbiting electron is an integral multiple of $h/2\pi$. The first postulate stated that $mvr = \frac{nh}{2\pi}$. The classical force due to the electrostatic attraction must be $\frac{mv^2}{r} = \frac{Ze^2}{r^2}$. Z is the number of positive charges in the nucleus (atomic number); e is the elementary unit of charge; r is the radius of the



BOHR ATOM TRANSITIONS: Those transitions for which $n_1 = 2$ and $n_2 = 3, 4,$ correspond to Balmer spectral lines. The Paschen series consists of lines emitted when an electron falls from a higher (or less negative) energy orbit to the third orbit ($n_1 = 3$). The Lyman series is emitted in transitions to the lowest state. Balmer lines are in the visible spectrum; Paschen lines are in the infrared; Lyman lines are ultraviolet. (most)

14 The expression for V (potential energy) of the electron is $- Z e^2/r$ because of the reference used for zero potential energy. Assume that the electron has zero potential when r is infinite. Since the nucleus attracts the electron, then as the electron approaches closer (r decreases) it loses potential energy with respect to the nucleus. This is consistent with the fact that we must do work on an electron to increase its potential; that is, to carry it out toward infinity.

(circular, let us assume) orbit. Combining the two equations by eliminating v gives the resulting expression for r: $r = \frac{n^2h^2}{4\pi^2 Ze^2m}$. The total energy is E=T+V, the sum of kinetic and potential. In terms of atomic properties, $E = \frac{mv^2}{2} - \frac{Ze^2}{r} = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$. Substituting for r from the above equation, we have an expression for the energy of the n^{th} state, which is $E_n = -\frac{Z^2e^4 2\pi^2 m}{n^2 h^2}$. Then the energy due to a transition is the difference of two such terms, or, in detail it is $E_{n_2} - E_{n_1} = -\frac{2\pi^2 m Z^2 e^4}{h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$ Now, since $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ holds for spectral lines of hydrogen, and $\frac{1}{\lambda} = \frac{\nu}{c}$ for light, as well as Einstein's $E = h\nu$ then it is found that $\frac{\nu}{c} = \frac{E}{hc}$ Also, Bohr's atom should emit the proper frequencies, provided $R = \frac{2\pi^2 e^4 m}{ch^3}$. The value of the Rydberg constant R computed from e, m, h, and c agreed well with the empirical value.

By the year 1923 it became clear that light (more generally, electromagnetic radiations) exhibited a dual nature. The "wave nature" explained interference, diffraction, refraction and polarization. On the other hand, the photoelectric effect, black-body radiation, and the Compton effect seemed to force on physicists light's "particle personality". If one asked him, "Is light a wave or a particle", the physicist was likely to answer, "Yes".

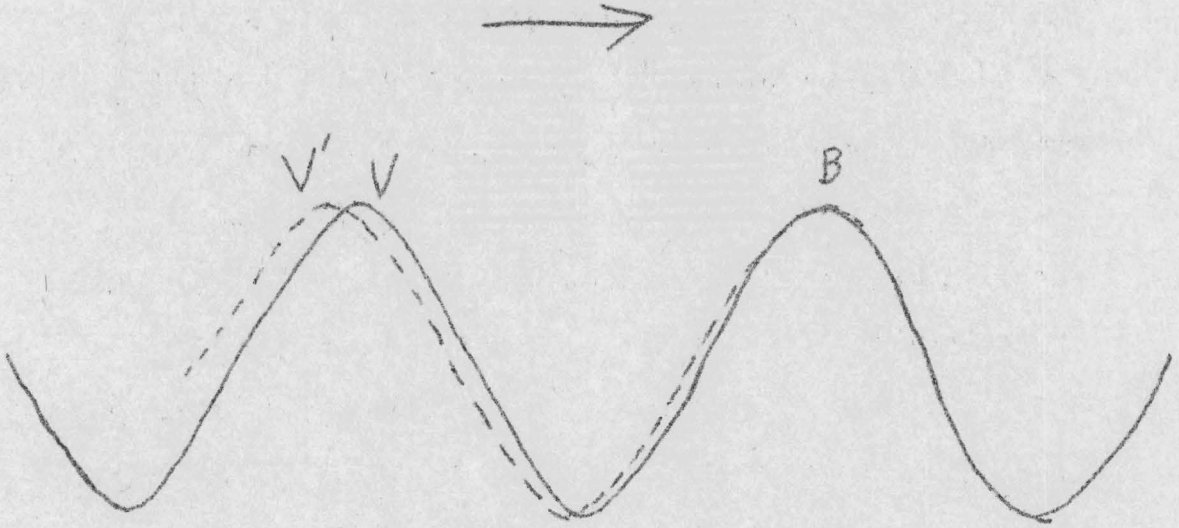
About that time, Louis de Broglie proposed that matter too should demonstrate a wave-particle nature. From relativity considerations, he demonstrated what would be the wave properties of matter. He examined the energy and momentum of photons. According to Planck, Einstein and Millikan, and Compton, the energy of a photon was hv. Also, according to Einstein, $E = h\nu = mc^2$ if a photon could be thought of as having an equivalent mass. Since light involves waves, though, $c = \nu\lambda$ as for any other waves. Then $h\nu = h c/\lambda = mc^2$ If a photon had any momentum ($p = mc$) it would have to be $p = \frac{h}{\lambda} = \frac{h\nu}{c}$

De Broglie suggested that if <u>matter waves</u> existed, that the momentum of (say, an electron) would be $mv = h/\lambda$ These matter waves would have a wave-length $\lambda = h/mv$ What is this matter wave like? If we let w represent the velocity of this (de Broglie) wave, and v represent the velocity of the electron, it turns out that $vw = c^2$ Since the energy travels with the particle, not necessarily with the wave this is not impossible.

The relation $vw = c^2$ seems at first incredible. This would say that an electron traveling with a velocity v less than c has associated with it a "matter wave" traveling faster than light in vacuum. But, where periodic waves are concerned, this is not a new concept. There is more than one velocity associated with periodic waves. Suppose one examines a small group of water waves traveling on a surface. It is easily observed that the group travels at a certain constant speed. This is called that wave's "group velocity". But a single wave-crest may be observed to move forward within the group. Thus, a single wave travels faster than the group velocity. The greater velocity here is called the "phase velocity". The explanation for this occurrence was given by Stokes.

Suppose that the waves were actually made up of two superposed waves of slightly different wave-length. The resultant of the two will give our wave group. If both of the superposed waves travel at the same speed, then the resultant wave travels at that speed, too. But if the longer wave moves faster than the shorter, then the resultant waves "back up" with respect to the original waves. That is, the group-velocity is less than that of the original wave.

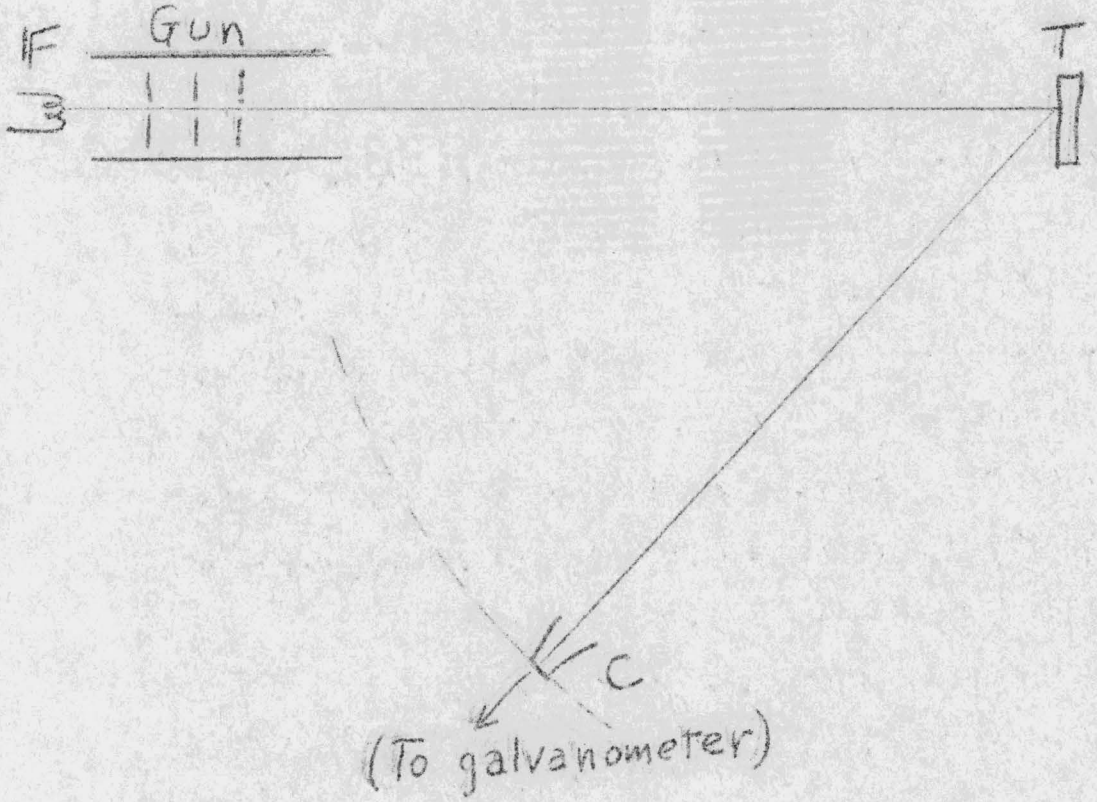
This may be seen clearly from the following diagram and analysis. The wave-train of length $\lambda' > \lambda$ travels



Superposed wave-Trains

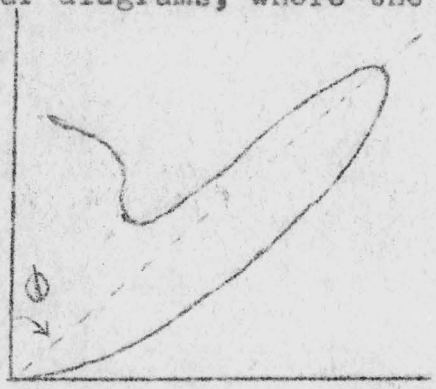
at a speed $V' > V$. The crest V' approaches V at a velocity $V' - V$. Let T be the time required for V' to overtake V. When this has happened, the center of the resultant wave group will have moved from B to the left by the amount of one wave-length, with respect to the λ-waves. Then $(V'-V)T = \lambda' - \lambda$ or $T = 1/\frac{d\nu}{d\lambda}$. In the time T, however, the λ-train has moved forward a distance VT. Therefore the center of the group has moved forward by $VT - \lambda$. But $VT - \lambda = \left(V - \lambda \frac{d\nu}{d\lambda}\right) T$. The group velocity then is $U = \frac{VT-\lambda}{T} = \left(V - \lambda \frac{d\nu}{d\pi}\right)$. In cases of no dispersion, or if $d\nu/d\lambda = 0$, then U = V. Otherwise, the group may travel slower than V. It turns out that the speed of light as was directly measured by Michelson and others is actually the group velocity of the light waves. Up on dispersion, the group velocity of the light waves differs from their phase velocity. Matter waves could behave in similar fashion.

Experimental evidence confirming the existence of matter waves came in 1927. Davisson and Germer of Bell Telephone Laboratories made the first discovery published. Their work was with the reflection of electrons from a single crystal of nickel. Their experiments showed for one thing that a beam of electrons striking a crystal surface were deffracted by the regular array of atoms, much like X rays. Diffraction suggested waves to them. So Davisson and Germer determined to test whether the diffraction was according to the deBroglie waves associated with electrons.



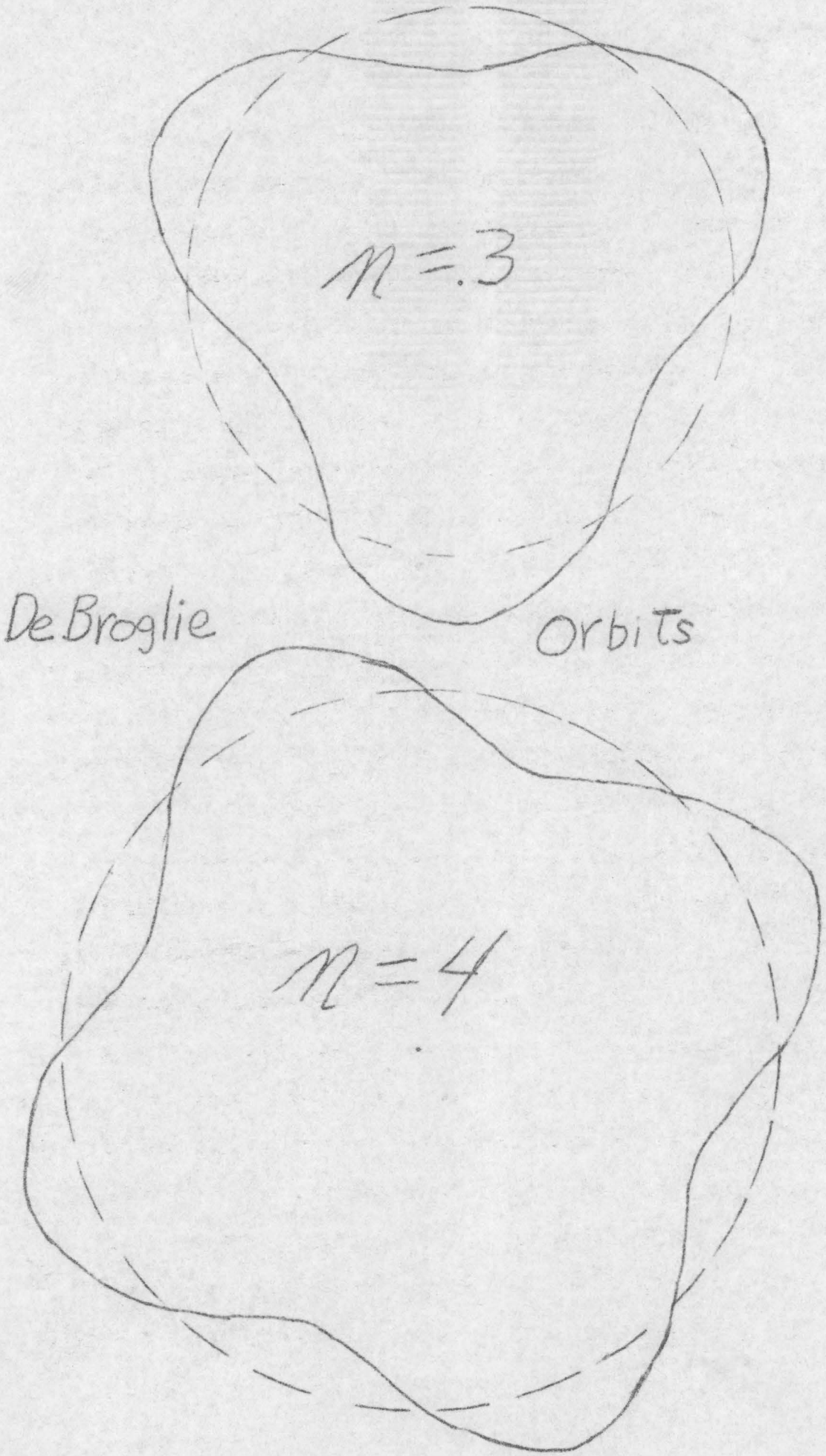
Schematic of Davisson-Germer Experiment

We now refer to the sketch of their experimental set-up. The electron gun boiled off and accelerated electrons at desired voltages. The crystal at T reflected the beam of electrons. At C was a movable collector leading to a galvanometer. C could be rotated about the T-axis through an angle ϕ. C could also be moved about the axis FT through an angle θ. Davisson and Germer moved the collector through angles of θ and found the current to vary periodically with θ. Then they fixed θ for a maximum current and varied ϕ only. The results are expressed by polar diagrams, where the radius vector is proportional to the current. When 54-volt electrons were used, a peak current occurred at an angle of 50°. Slower or faster electrons from 40 v. to 68 v. gave less "spur" or none at all for the same value of ϕ. Again, when 181 v. electrons were used, a similar peak occurred at an angle of $\phi = 55°$. Other strong beams were found for other azimuth (θ) values, at different voltages. Here was a strong suggestion of the presence of waves. Let us take the example for which $\phi = 50°$ and V = 54 v. Since only surface atoms of nickel were being utilized, Davisson and Germer used $n\lambda = d \sin$ to relate the angle

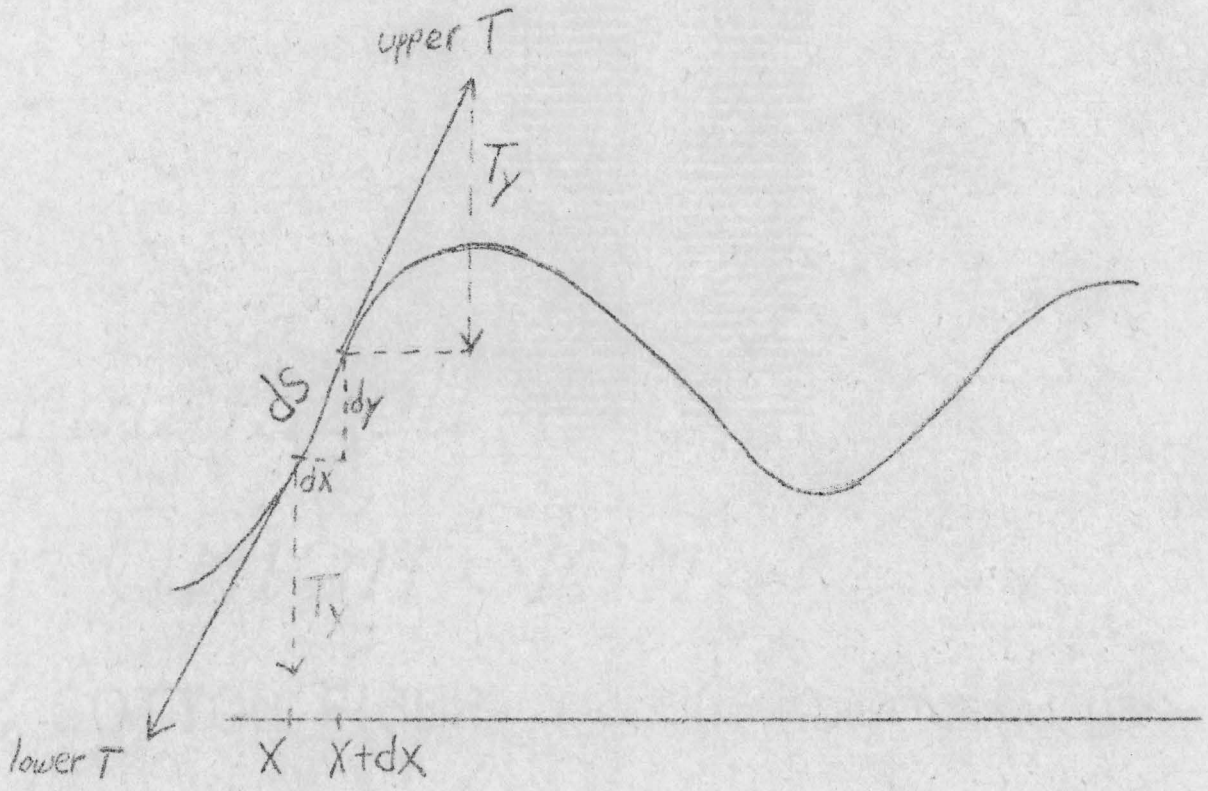


of diffraction to the crystal spacing and the "waves". The Bragg formula for X rays is $n\lambda = 2\,d \sin\Phi$ where layers of atoms in a crystal are being used. The azimuth of the crystal was such that the crystal spacing was $d = 2.15 \times 10^{-8}$cm. Taking this to be for $n = 1$, we have $\lambda = 2.15 \times 10^{-8} \times \sin 50^{\circ} = 2.15 \times 10^{-8}$cm. $\times$ $.7660 = 1.65 \times 10^{-8}$cm. for the waves. The second- order value ($n = 2$) is $\lambda = 2.15 \times 10^{-8}$cm. $\times$ $.8192/2$. The de Broglie wave-length is $.88 \times 10^{-8}$cm., about half that of the first-order diffraction. Using the de Broglie equation $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2Vem}}$ where V is the potential and e the electronic charge. The first-order value is (in MKS units) $\lambda = \frac{6.62 \times 10^{-34}\text{joule sec.}}{2 \times 54\text{v.} \times 1.6\times10^{-19}\text{coul.}\times 9.11\times10^{-31}\text{kg.}}$ $= 1.67 \times 10^{-10}$m. A similar calculation for the second order yields $\lambda = .91 \times 10^{-8}$cm. Both are in good agreement with Davisson and Germer's experimental values. In nineteen cases, they found similar agreement.

Kikuchi of Japan passed electrons through very thin sheets of mica and obtained the Laue diffraction patterns so familiar from X ray diffraction. The results were in agreement with the de Broglie wave-length for electrons. Diffraction of electrons by thin metallic films done by G. P. Thomson of England also confirmed the existence of the electron waves that de Broglie had predicted.


n = 3
De Broglie
Orbits
n = 4

About a year a fter de Broglie's initial work, the form of the new "wave mechanics" was made more complete and rigorous by Schroedinger. We shall return to his mathematical approach later. Now we can examine some of the uses de Broglie waves have in regard to the Bohr atom. One of Bohr's postulates amounts to saying that $mvr = \frac{nh}{2\pi}$ for the circular orbits. Combining this with the expression for the matter-wave-length $\lambda = \frac{h}{mv}$, results in $\lambda = \frac{2\pi r}{n}$ or $n\lambda = 2\pi r$. The last equation shows that Bohr's condition for a stable orbit is inter-p reted by wave mechanics as making it necessary that such an orbit contains an integral number of wave-lengths. In other words, an electron in a stable orbit always has matter-waves associated with it that are standing waves. For the Bohr quantum number n = 1, the orbit circumference fits one wave-length; for n = 2, two wave-lengths, and so on. Besides that, these waves could help to explain a transition between states--something the Bohr theory did not attempt to do. When an electron in a hydrogen atom made a change from energy state E_2 to state E_1, a quantum of energy hv was emitted. The de Broglie wave frequencies ν_2 and ν_1 for the standing waves in each state could give rise to the emitted radiation according to the "beat frequency" condition $\nu = \nu_2 - \nu_1$. Both this condition and the equation $\nu = \frac{E_2}{h} - \frac{E_1}{h}$ hold simultaneously if $\nu_2 = \frac{E_2}{h} + \frac{K}{h}$ and $\nu_1 = \frac{E_1}{h} + \frac{K}{h}$ where K is some constant. Take E + K to



Vibrating String

mean the total energy E_t of the electron. This means that for the matter waves $f = \frac{E_r}{h}$ If the waves travel with a velocity $w = f\lambda = \frac{E_r}{h} \cdot \frac{h}{mv} = \frac{E_r}{mv}$ then $E_t = m c^2$ leads to $w = c^2/v$. This is a characteristic to be expected of the matter waves. When one considers the bending (refraction) of electrons by a changing electric field and treats the problem according to Snell's law for waves, the result w = a constant/v again appears.

Schroedinger formulated the matter-wave concept into the mathematics of wave mechanics. He began by considering the mechanics of oscillation of a quantity. We may use a vibrating string as a model to show the development. Consider the forces on an element dS. Now the upper T = the lower T; so the upper T_y = the lower T_y because the x-components are in equilibrium. By Newton's law $\Sigma T_y = m a_y$ $T_{y(x+dx)} - T_{y(x)}$ or $\mu\, dS\, \partial^2 y/\partial t^2$, where μ = m/dS, the linear density. By Taylor's series $f(x+dx) = f(x) + f'dx + f''\frac{dx^2}{2!} \ldots$ We use the first two terms for differential changes. So $T_{y(x)} + \frac{\partial T_y}{\partial x} dx - T_{y(x)} = \frac{\partial T_y}{\partial x} dx$ or $\frac{\partial T_y}{\partial x} dx = \mu\, dS\, \frac{\partial^2 y}{\partial t^2}$. Now, examine the right member only. For small-amplitude waves, dx $\doteq$ dS. The right member becomes $\mu\, dx\, \frac{\partial^2 y}{\partial t^2}$. Now, turn to the similar triangles of T and dS. $\frac{T_y}{T} = \frac{\partial y}{\partial x}$ or $T_y = T \frac{\partial y}{\partial x}$ and since T is a constant,

becomes $\frac{\partial^2 u}{\partial x^2} + \left(\frac{2\pi p(x)}{h}\right)^2 u = 0$

When conservative forces are present (as in an atom with a central-force field) $E = p^2/2m + V$ expresses the energy. Then $p^2 = 2m(E-V)$, substituted into the wave equation results in $\frac{\partial^2 u}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)u = 0$

This is actually the one-dimensional Schroedinger equation. The multi-dimensional equation has the same form. It is $\nabla^2 u + \frac{8\pi^2 m}{h^2}(E-V)u = 0$, the differential equation describing standing matter waves in space. For non-standing waves, such as would be the case during a transition of an electron in the hydrogen atom, the equation takes the form $-\frac{h^2}{8\pi^2 m}\nabla^2\psi + V\psi = -\frac{h}{2\pi i}\frac{\partial \psi}{\partial t}$ where $\psi = u \cdot T$, T being a complex function of time.

Now, let us apply the Schroedinger equation to the hydrogen atom. The electron is in the field of the nuclear proton. The potential V of the electron is $V = -\frac{Z e^2}{r}$. The total energy (kinetic plus potential) is then $E = \frac{p^2}{2m} - \frac{Z e^2}{r}$.

Next, we shall express the Schroedinger equation in polar coordinates, those that apply best to the hydrogen atom. This change of coordinates affects the Laplacian operator ∇^2. To change from rectangular to polar coordinates, we make the substitutions:
$x = r \sin\theta \cos\phi$; $y = r \sin\theta \sin\phi$; $z = r \cos\theta$.
The operator $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ or, in polar coordinates,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Now, assume that the wave function Ψ is a product of three functions: $R(r)\Theta(\theta)\Phi(\phi)$. This is a standard way of separating the variables r, θ and ϕ. Now, we take :

$$\left[\nabla^2 + \frac{2m}{\hbar^2}\left(E + \frac{Ze^2}{r}\right)\right]\Psi = 0$$

and express it in polar coordinates, and divide it through by $\Psi = R\Theta\Phi$.

$$\left[\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2m}{\hbar^2}\left(E + \frac{Ze^2}{r}\right)\right] +$$

$$\frac{1}{r^2}\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)\right] + \frac{1}{r^2\sin^2\theta}\left(\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}\right) = 0$$

In the last term, $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}$ is a function of ϕ only. But in the equation, this term can be equal to the other two terms; they are functions of r and θ only. This

can be so only if the terms are all constants: $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -m^2$ (a constant), for which the solution $\Phi = e^{\pm im\phi}$ or $\cos m\phi \pm i \sin m\phi$. Since Φ represents a physical wave of some kind, then Φ has the same value at positions ϕ, $\phi + 2\pi$, ..., $\phi + 2n\pi$, ... Thus, if $\Phi = e^{\pm im\phi} = \cdots$, then $m = 0, \pm 1, \pm 2, \ldots$. The m is called the magnetic quantum number.

The last two terms of the Schroedinger equation are $\frac{1}{r^2}\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta}\right]$. The expression in brackets is a function of θ only. It is equal to a function of r only. Then the bracketed quantity must be another constant. Call this constant $\ell(\ell+1)$. There are finite solutions Θ provided $\ell = 0, 1, 2, \ldots$. The solutions are called the Legendre polynomials. The result is that $\ell \geq |m| \geq 0$, for the first two quantum numbers. When we examine the R part of the Schroedinger equation and use $X = R/r$, $x = kr$, where $k^2 = -2mE/\hbar^2$ (h-bar squared: $h/2\pi$), a solution is $X = A\, x^n e^{-x}$, for electrons close to the nucleus.

When this solution is tried in the equation, and $\ell(\ell+1)$ is used in the Φ-term, the conditions $n = 1, 2, 3, \ldots$ and $n = \ell + 1$ result. This condition on the third quantum number n gives the correct energy levels for the hydrogen atom.

Because X above has other solutions, the quantum number $n = \ell \pm 1 + \nu$ ($\nu = 0, 1, 2, \ldots$). This makes ℓ and n really independent quantum numbers. Then $n > \ell \geq 0$.

The quantum number n is called the principal or orbital quantum number; ℓ is the azimuthal or angular-momentum quantum number and m is the magnetic quantum number (the quantum of the z-component of the angular momentum of the electron). The Stern-Gerlach experiment with hydrogen reveals a fourth quantum number. A given spectral line was observed to split into two lines, equally-spaced from the normal line, as a result of a non-uniform magnetic field. All the previously-known conditions on the other three quantum numbers predicted that the line should split into three, including one in the middle, undeviated position. The assumption of a spin quantum number m_s, indicating that the electron may have either of two spins about its own axis, such that $m_s = \pm \frac{1}{2}$, accounts for the observations quantitatively.

Summarized, the quantum conditions on atomic electrons are:

1. n, ℓ, m are all integers; $m_s = \pm\frac{1}{2}$
2. $n > \ell \geq 0$
3. $-\ell \leq m \leq \ell$

Then there are $(2\ell + 1)$ values of m for each ℓ. There are $2(2\ell + 1)$ combinations of m and m_s for each ℓ. There are (n - 1) values of ℓ for each n. Thus for each Bohr orbit (a given n), the number of possible states an electron may have is given by the quantum conditions.

Pauli was responsible for introducing the fourth or spin quantum number for the electron, and with it came the Exclusion Principle. In terms of the quantum numbers, the principle is stated as, 'No two electrons may have the same set of values of all four quantum numbers'. In other words, no two electrons in an atom may have the same energy-level. The principle has to follow from the quantum conditions, which were derived from Schroedinger's equation. For the quantum numbers constitute the only way of telling the difference between one atomic state and another. As far as any test can possibly determine, a given set of four numbers shows a given electron; another set of numbers is the only way possible to describe another electron.

As we have indicated, the quantum conditions and the Pauli principle dictate the states an electron can have. Therefore, in atoms which have many electrons, each electron must fall in a different state. Next, we will show how all the electrons must be regimented in

ELECTRON QUANTUM STATES

State	$n=$	$l=$	$m_l=$	$m_s=$
1s	1	0	0	$+\frac{1}{2}$
			0	$-\frac{1}{2}$
2s	2	0	0	$+\frac{1}{2}$
			0	$-\frac{1}{2}$
2p	2	1	+1	$+\frac{1}{2}$
			+1	$-\frac{1}{2}$
			0	$+\frac{1}{2}$
			0	$-\frac{1}{2}$
			-1	$+\frac{1}{2}$
			-1	$-\frac{1}{2}$
3s	3	0	0	$+\frac{1}{2}$
			0	$-\frac{1}{2}$
3p	3	1	+1	$+\frac{1}{2}$
			+1	$-\frac{1}{2}$
			0	$+\frac{1}{2}$
			0	$-\frac{1}{2}$
			-1	$+\frac{1}{2}$
			-1	$-\frac{1}{2}$
3d	3	2	+2	$+\frac{1}{2}$
			+2	$-\frac{1}{2}$
			+1	$+\frac{1}{2}$
			+1	$-\frac{1}{2}$
			0	$+\frac{1}{2}$
			0	$-\frac{1}{2}$
			-1	$+\frac{1}{2}$
			-1	$-\frac{1}{2}$
			-2	$+\frac{1}{2}$
			-2	$-\frac{1}{2}$

the various atoms. We can easily show how the periodic table of the elements follows from quantum mechanics. When n = 1 (first Bohr orbit), ℓ = 0, m = 0, $m_s = \pm\frac{1}{2}$; then there are two opposite-spin electrons in this state. When n = 2, ℓ = 0, then m = 0, $m_s = \pm\frac{1}{2}$, and again there are two electrons. The condition ℓ = 0 defines an s-state; n = 1, ℓ = 0 is the 1s state; n = 2, ℓ = 0 is the 2s state. All s-states have no more than two electrons. The condition ℓ = 1 defines the p-state.

When n = 2, ℓ = 1, there are three possible values of m (-1, 0, +1) and again, the two values of m_s. Thus, there are six electrons in the 2p state we have just described. We should say there are no more than six electrons in this sub-shell, because some atoms may not have enough to fill the state.

We see then, that for n=2, there are eight electrons, maximum number for the second Bohr orbit.

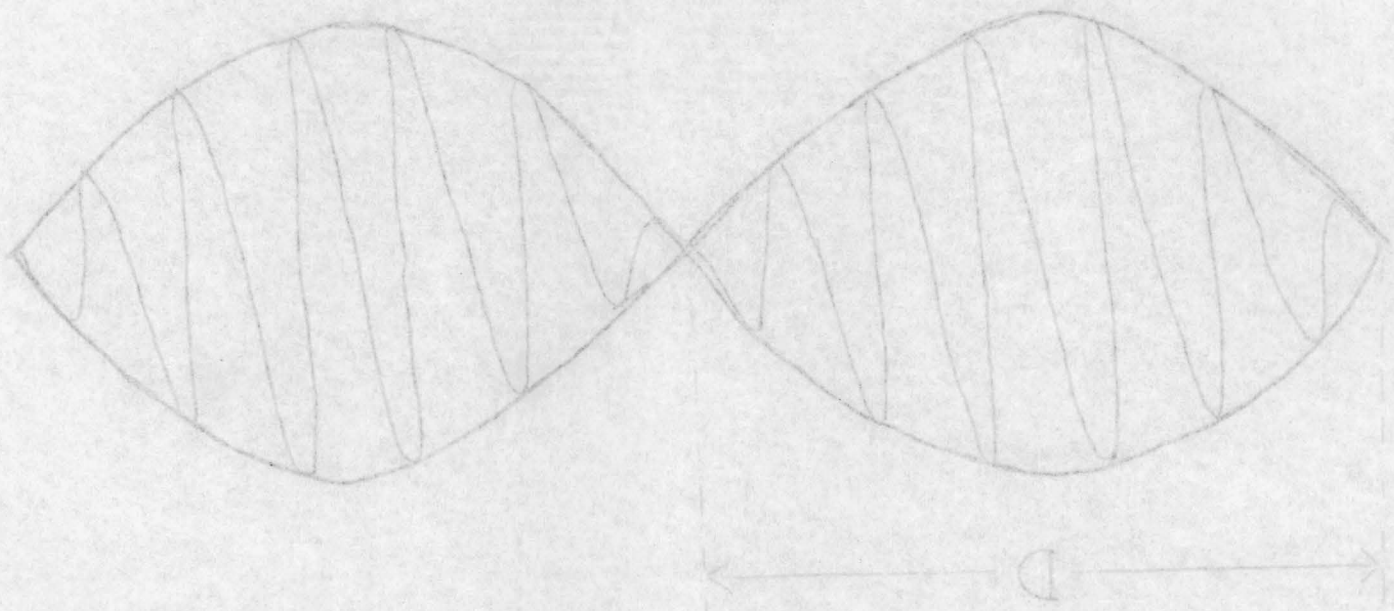
When n = 3, ℓ may have values of 0, 1, or 2. The last condition defines the d-state. When n = 4, there can exist an f-state, for which ℓ = 3. Applying the quantum conditions reveals that a d-state can have no more than ten electrons; an f-state cannot allow more then fourteen.

(PARTIAL) PERIODIC TABLE OF THE ELEMENTS

(shells) n=	1	2		3			4		
(subshells) =	0	0	1	0	1	2	0	1	
1 H	1s								
2 He	$1s^2$								
3Li	$1s^2$	2s							
4 Be	"	$2s^2$							
5 B	"	"	2p						
6 C	"	"	$2p^2$						
7 N	"	"	$2p^3$						
8 O	"	"	$2p^4$						
9 F	"	"	$2p^5$						
10 Ne	"	"	$2p^6$						
11 Na	"	"	"	3s					
12 Mg	"	"	"	$3s^2$					
13 Al	"	"	"	"	3p				
14 Si	"	"	"	"	$3p^2$				
15 P	"	"	"	"	$3p^3$				
16 S	"	"	"	"	$3p^4$				
17 Cl	"	"	"	"	$3p^5$				
18 A	"	"	"	"	$3p^6$				
19 K	"	"	"	"	"		4s		
20 Ca	"	"	"	"	"		$4s^2$		
21 Sc	"	"	"	"	"	3d	"		
22 Ti	"	"	"	"	"	$3d^2$	"		
23 V	"	"	"	"	"	$3d^3$	"		
24 Cr	"	"	"	"	"	$3d^4$	"		
25 Mn	"	"	"	"	"	$3d^5$	"		
26 Fe	"	"	"	"	"	$3d^6$	"		
27 Co	"	"	"	"	"	$3d^7$	"		
28 Ni	"	"	"	"	"	$3d^8$	"		
29 Cu	"	"	"	"	"	$3d^{10}$	4s		
30 Zn	"	"	"	"	"	$3d^{10}$	$4s^2$		
31 Ga	"	"	"	"	"	"	"	4p	
32 Ge	"	"	"	"	"	"	"	$4p^2$	
33 As	"	"	"	"	"	"	"	$4p^3$	
34Se	"	"	"	"	"	"	"	$4p^4$	
35 Br	"	"	"	"	"	"	"	$4p^5$	
36 Kr	"	"	"	"	"	"	"	$4p^6$	

There is a general rule for the order of filling of subshells. They fill in order of increasing (n + l); but for constant (n + l) the subshells of lowest n fill first. There are a few exceptions to this.

In the partial periodic table of the elements, through the fourth period, the order of filling is demonstrated. The superscripts on the s, p, d, are to denote the number of electrons in that subshell; the s-state has either one or two, the p-state has from one up to six, etc. .


D

We have seen how wave mechanics can make correct predictions about the hydrogen atom, and even the structure of the periodic table. Now, let us return to the mechanics of a single free particle. Earlier, we discussed (pp. 28, 29) properties of superposed waves. Suppose two such waves interfere in such a manner as to produce envelopes or "packets" of resultant waves as shown here. Each envelope corresponds to a certain location of the particle. The broadness of the envelope determines the uncertainty of position of the particle. If D is the width of the envelope, then $\Delta x = D/2$. But, for wave-packets made up of two simple waves of λ_1 and λ_2, such that $\lambda_1 \simeq \lambda_2 \simeq \lambda$, W, the wave-velocity is given by $W = D\Delta\nu$. Then $D = \frac{W}{\Delta\nu} \simeq \frac{1}{\Delta(\frac{1}{\lambda})}$. These are the de Broglie waves, and $\lambda = h/p$. Then $D = \frac{1}{\Delta(\frac{p}{h})}$ or $2\Delta x \simeq \frac{h}{\Delta p}$. Finally, $\Delta x \cdot \Delta p \simeq \frac{h}{2}$. The uncertainty (Δp) of particle momentum corresponds to a spread of wave-length $(\Delta \frac{1}{\lambda})$. When such a spread, or greater difference of λ_1 and λ_2 of the superposed waves, occurs, it makes a narrower envelope. This means a more definite position of the particle. But if $\Delta(\frac{1}{\lambda})$ is small, Δp is small and the superposed waves are nearly the same in wave-length. This makes the resultant envelope very long, and the uncertainty of position (Δx) becomes very large.

The relation $\Delta x \cdot \Delta p \simeq \frac{h}{2}$, or, more precisely $\Delta x \cdot \Delta p = \frac{h}{2\pi}$, is called Heisenberg's Uncertainty Principle.

To get an idea of its application, let us apply the principle to two problems--one atomic in size and another macroscopic in size. First, the macroscopic example--a bullet in flight. Suppose we are able to determine its position to about .1 mm.. Then, according to the uncertainty principle,

$$\Delta p \simeq \frac{\hbar}{\Delta x} \simeq \frac{10^{-27}\ \text{erg-sec.}}{10^{-2}\ \text{cm.}} \simeq 10^{-25}\ \text{gm.-cm/sec.}$$

If the mass is 20 gm., $\Delta v = \frac{\Delta p}{m} \simeq \frac{10^{-25}}{20} \simeq 10^{-24}$ cm/sec.

In a velocity of about 10^4 cm/sec., this is by far an unmeasurable amount.

Now, imagine that we try to locate an electron with atomic precision. Let the electron's position be known to a fraction of an atom's diameter--10^{-9} cm. . This would require a microscope that utilizes gamma rays to "see". At least one photon ($h\nu$) is needed to allow detection, and it must recoil back to us from the electron. This would impart a Compton momentum (pp. 22, 23) to the electron. The amount to assign to electron momentum depends on the angle of collision, but it would be some fraction of the initial momentum of the photon: $\Delta p \simeq \frac{h}{\lambda} \simeq \frac{10^{-27}\ \text{erg-sec.}}{10^{-9}\ \text{cm.}} \simeq 10^{-22}\ \text{gm.-cm/sec.}$

The uncertainty in electron velocity would be a fraction of: $\frac{\Delta p}{m} \simeq \frac{10^{-22}\ \text{gm-cm/sec}}{10^{-29}\ \text{gm.}} \simeq 10^{7}\ \text{cm/sec.}$

If we narrow the aperture to reduce the uncertainty in momentum, the resolving power is reduced, thus limiting the knowledge of position of the electron. We cannot

fix the position without sacrificing a knowledge of momentum; and we cannot precisely predict the momentum without increasing the uncertainty of position.

In the Schroedinger equation, the Ψ was called a "wave-function"--a mathematical symbol, operated on by the La placian ∇^2. Now we will consider the physical significance of the Ψ. The solution of the Schroedinger equation is a complex function of time: $\Psi = C\, e^{-(2\pi i/h)(Et-px)}$. This corresponds to the situation where Ψ would be the <u>amplitude</u> of oscillations traveling with time--waves like the envelope we considered above. The <u>intensity</u> of such a wave is given by the amplitude squared (Ψ^2. Since this amplitude is complex, that could lead to a negative intensity, something physically meaningless. Instead of Ψ^2 the intensity is or $|\psi|^2$; the Ψ^* being the complex conjugate, $\psi^*\psi = |\psi|^2$.

Max Born interpreted the position of a particle in terms of Ψ. At a given time, the particle could be found anywhere within the packet, where $\Psi \neq 0$. The probability of finding the particle in a given position is proportional to $|\psi|^2$ (the wave intensity there). Another way of saying this is that the <u>probability density</u> at a point is $|\psi|^2$. The probability of finding a particle within any element of volume dx dy dz is $|\psi|^2\, dx\, dy\, dz$. Ψ is therefore sometimes called the probability amplitude for the particle's postion. Since the probability of finding a particle somewhere is 1, then $\iiint |\psi|^2\, dx\, dy\, dz = 1$.

In the solution $\psi = C e^{-2\pi i/h (Et - px)}$ where $E = p^2/2m$, if C is a constant and p is a constant (that is, if we have complete knowledge of the momentum) then the function corresponds to an infinite wave-train. In other words, $\iiint |\psi|^2 dx\, dy\, dz = \infty$ and we have an infinitely long wave-packet. This is another expression of the Heisenberg uncertainty principle. By assigning zero uncertainty to momentum, we have no knowledge at all of position.

Heisenberg developed matrix mechanics to describe atomic systems, where classical mechanics failed. The uncertainty principle is one important conclusion. Schroedinger's wave mechanics give the same essential results. In fact, Schroedinger showed that wave mechanics and matrix mechanics are equivalent. The wave equation is easier to work with. Both forms of the new quantum mechanics are based on the measured observables of experiments--not on <u>a priori</u> mechanical models or concepts which may be unmeasurable. An electron (pictured as a definite particle) will never be seen because it is unseeable. Quantum mechanics emphasizes that any physical theory or model--mathematical or otherwise--is only useful in so far as it can make correct predictions about the outcome of further experiments. Quantum mechanics has proved to be useful in making correct predictions not only in atomic systems but also in complex nuclear processes.

APPENDIX

(Taken from Heathcote's, Nobel Prize Winners in Physics, pp. 153-165; from Richtmyer's, Introduction to Modern Physics, 1928 ed., pp. 229-241; and from Ruark's and Urey's, Atoms, Molecules and Quanta, 1930 ed., pp. 12, 57-59.)

Clausius had defined entropy as $S = \frac{dQ}{T}$ where dQ is a small amount of energy transferred in a heat exchange. The value of the entropy S is zero for reversible processes, where a cyclical process would bring the system back to the initial state. Furthermore, S increases in irreversible processes , those that cannot be retraced. Planck regarded natural processes as irreversible.

First, Planck started with the experimental laws of Rayliegh and Wien and fitted them into a theory that included both laws. The energy, Planck assumed, was radiated by the oscillations of many simple oscillators. His expression for the energy of an oscillator was $E = a \cdot e^{-b/T}$ where a is Wien's C_1/λ^5 and b is Wien's C_2/λ. The Rayleigh law Planck writes as $E = cT$ where c is Rayleigh's K/λ^4 Then $\frac{dS}{dE} = \frac{1}{T}$ is a form of the definition of entropy. Differentiating, $\frac{d^2S}{dE^2} = \frac{-\frac{1}{T^2}}{dE/dT}$ (Eq. 1)

If $E = a e^{-\frac{b}{T}}$ then $dE/dT = bE/T^2$ (Eq. 2)

and if $E = cT$ then $dE/dT = c$ (Eq. 3)

Substituting Eq. 2 into Eq. 1 gives $\frac{1}{d^2S/dE^2} = -bE$

Substituting Eq. 3 into Eq. 1 gives $\frac{1}{d^2S/dE^2} = -\frac{c}{T^2} = -\frac{E^2}{c}$

which gives the results in the middle of page 18.

APPENDIX

In his theoretical development of the law, Planck did not rely on the experimental relations to begin. Instead, he calculated the entropy of a resonator (oscillator) as a function of its energy. The entropy S_n of a system of N resonators is connected with the probability W of the state of the system by Boltzmann's relation $S_n = k \log W$. Let the combined energy of N resonators be U_n. Then , to get an expression for the probability W of any particular distribution of this total energy, he had to find the number of ways in which the total energy can be distributed among the resonators. According to accepted ideas of energy, the problem of distributing the total energy U_n among N resonators is that of dividing it into <u>any</u> quantities. This makes the problem insoluble, because there are an infinite number of possibilities. Planck, however, reduced it to the soluble problem of distributing U_n into P elements of energy each equal to e. Then $U_n = P\,e$. No energy is found in any resonator, except in multiples of e.

It turns out that if N or P is very large, as is the case where N in some way measures the number of atoms and P must be large for e is very small, then the number of possible distributions is approximately $\frac{(N+P)^{N+P}}{N^N \times P^P}$

Taking the number of possible distributions as a measure of the probability of the system, the Boltzmann equation becomes

$$S_n = k \log W = k \log \frac{(N+P)^{N+P}}{N^N \times P^P}$$

or

$$S_n = k\left[(N+P)\log(N+P) - N\log N - P\log P\right]$$

APPENDIX

The next step is to eliminate P. Let U be the average energy of a single resonator. Then $U_n = U N = P e$ or $P = \frac{U N}{e}$

Therefore

$$S_n = K\left[\left(N+\frac{UN}{e}\right)\log\left(N+\frac{UN}{e}\right) - N\log N - \frac{UN}{e}\log\frac{UN}{e}\right]$$

$$= KN\left[\left(1+\frac{U}{e}\right)\log N\left(1+\frac{U}{e}\right) - \log N - \frac{U}{e}\log N\frac{U}{e}\right]$$

$$= KN\left[\left(1+\frac{U}{e}\right)\left\{\log\left(1+\frac{U}{e}\right)+\log N\right\} - \log N - \frac{U}{e}\left\{\log\frac{U}{e}+\log N\right\}\right]$$

$$= KN\left[\left(1+\frac{U}{e}\right)\log\left(1+\frac{U}{e}\right) - \frac{U}{e}\log\frac{U}{e}\right]$$

finally, because all the log N terms cancel out.

Then the entropy of a single resonator is given by

$$S = K\left[\left(1+\frac{U}{e}\right)\log\left(1+\frac{U}{e}\right) - \frac{U}{e}\log\frac{U}{e}\right]$$

Next, using Wien's displacement law $\lambda T = \text{const.}$ and the definition of entropy, it follows that $\frac{dS}{dU} = \frac{1}{T} = \frac{\lambda}{\text{Const.}}$

or, in terms of frequency, $\frac{dS}{dU} = \frac{c}{\nu \times \text{Const.}}$

because $\lambda\nu = c$, the velocity of light.

Therefore $dS = \frac{c \cdot dU}{\nu \times \text{Const.}}$ and S is a function of U/ν alone.

This means the expression above for S must contain only U/ν and constants. To assure this, Planck let $e = h\nu$ where h is a constant, giving $S = K\left[\left(1+\frac{U}{h\nu}\right)\log\left(1+\frac{U}{h\nu}\right) - \frac{U}{h\nu}\log\frac{U}{h\nu}\right]$

Differentiation with respect to U gives

$$\frac{1}{T} = \frac{dS}{dU} = \frac{K}{h\nu}\log\left(1+\frac{h\nu}{U}\right)$$

making $\frac{h\nu}{KT} = \log\left(1+\frac{h\nu}{U}\right)$ or $1+\frac{h\nu}{U} = e^{h\nu/KT}$

Finally, $$U = \frac{h\nu}{e^{h\nu/KT}-1}$$

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